#### AN ABSTRACT OF THE THESIS OF

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in Chemical Oceanography presented on May 4, 1970
CHEMICO-OCEANOGRAPHICAL PARAMETERS OF THE

CENTRAL NORTH PACIFIC OCEAN

Abstract approved: \_Redacted for Privacy

Data from the Surveyor 1968 Spring cruise were used to study the vertical distribution of salinity, temperature, dissolved oxygen, apparent oxygen utilization, pH, alkalinity, specific alkalinity and percent saturation of calcite in two sections, one along 162°W from 35°N to 45°N and the other along 180°W from 35°N to 50°N. Data from this cruise and additional data from the Surveyor 1968 Fall cruise, YALOC 66 cruise (summer) (Barstow et al., 1968) and Boreas cruise (winter, 1966) (SIO reports, 1966) were used to study the distribution of salinity, temperature, apparent oxygen utilization, preformed phosphate and depth on the sigma-t surfaces of 26.8 and 27.3 in an area between 35°N and 52°N and 162°W and 155°E.

In both sections the vertical distribution of the physico-chemical parameters is such that in general there is a tendency for the isograms to slope upward from south to north following the same trend of the sigma-t surfaces. This indicates that mixing and advection

along the sigma-t surfaces play an important role on the distribution of these parameters.

AOU data from YALOC 66 cruise (summer) compared to that from Surveyor 1968 Spring cruise suggest that aeration by mixing, eddy diffusivity and conductivity takes place to more than 500 meters depth at about 50°N. It also suggests that the changes of organic primary production at the euphotic zone during different seasons of the year may affect to a great extent the AOU distribution on the 26.8 sigma-t surface and to a very small extent on the 27.3 sigma-t surface.

The direction of flow suggested by the AOU distribution on the 26.8 and 27.3 sigma-t surfaces was compared to that indicated by the acceleration potential contours on the  $d_t$  = 125 cl/ton and  $d_t$  = 80 cl/ton surfaces drawn by Reid (1965). The disagreements were explained in terms of mixing and possible gradients of primary production at the sea surface. On the 26.8 sigma-t surface a southward flow connecting the westward flow south of the Aleutian chain and the eastward flow farther south, between 175°E and 180°W is suggested by the AOU distribution but not by the acceleration potential contours. If the circulation pattern at this density surface is similar to that at the sea surface, this linkage is very likely to be real.

## Chemico-oceanographical Parameters of the Central North Pacific Ocean

by

Saúl Alvarez-Borrego

#### A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Master of Science

June 1970

APPROVED:

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Date thesis is presented May 4, 1970

Typed by Suelynn Williams for Saul Alvarez-Borrego

With love to my parents

Pedro Alvarez-Ortega and Dolores Borrego-De-Alvarez

With affection and admiration to

Dr. Norris W. Rakestraw

#### ACKNOWLEDGMENTS

I thank my major professor Dr. P. Kilho Park for his guidance throughout this study. I also would like to express my thanks to the Francis P. Shepard Foundation and the Instituto Nacional de la Investigación Científica de México for their support while working on my Master's degree program.

I extend additional thanks to Dr. Felix Favorite for his helpful criticisms. The discussions with Louis I. Gordon were very helpful.

I also want to thank Stephen Hager, Milton C. Cissell, David S. Ball, Jacques Pirson, Dennis Barstow, Peter Becker, the scientific personnel from the Pacific Oceanographic Research Laboratory at Seattle, Washington, and the officers and crew of the USC&GSS Surveyor for doing all the necessary work at sea during the Surveyor 68 Spring and Surveyor 68 Fall cruises.

I appreciate the help of Lynn Jones with the computer program and the comments of John Hawley and Charles H. Culberson regarding the study of calcium carbonate saturation.

I am indebted to Lynda Barstow for her helpful comments regarding the grammatical structure of this thesis and to Suelynn .
Williams for typing.

Finally, I want to express my sincere gratitude to my wife,

Esthela Elsie Millán-De-Alvarez, for continuously encouraging me
and for being patient while I was working on this thesis.

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## CHEMICO-OCEANOGRAPHICAL PARAMETERS OF THE CENTRAL NORTH PACIFIC OCEAN

#### I. INTRODUCTION

The North Pacific Ocean has been subjected to extensive oceanographic investigations. Since the formation of the International North Pacific Fisheries Commission there has been an intensive investigation of the ecological factors that affect the distribution of the economically important marine organisms that have their habitat in this part of the ocean. A great part of these studies have dealt with physical oceanographic problems and have provided an excellent framework for any other type of study.

Several authors (Dodimead, Favorite and Hirano, 1963; Reid, 1965; and others cited therein) have reviewed the literature concerned with the physical oceanography of the North Pacific Ocean.

Sverdrup, Johnson and Fleming (1942) mentioned that in the North Pacific Ocean one encounters a Subarctic Water mass at about 50°N characterized by an average temperature between 2° and 4°C. According to them salinity at the surface may be as low as 32.00% but increases to approximately 34.00% at a depth of a few hundred meters and below that depth increases slowly to about 34.65% at the bottom.

On the basis of data collected in the Northwestern Pacific from 1929 to 1954 Hirano (1958) was able to obtain general information on distributions of temperature and salinity as well as the flows and their circulations in this region for spring and summer.

Tully and Dodimead (1957), using data in the Northeast Pacific, identified Subarctic and Subtropic Waters. They showed that the

principal differences were in the properties and the structure of the upper layers.

The Subarctic Boundary between these two water masses is generally identified by a nearly vertical isohaline of 34.0% which extends from the surface to a depth of about 200 to 400 meters (Dodimead, Favorite and Hirano, 1963).

North of the boundary in the Subarctic Region, the salinity is at a minimum at the surface and increases with depth. The water column is characterized by a permanent halocline between approximately 100 and 200 meters depth above which a thermocline develops in summer and vanishes in winter. South of the boundary in the Subtropic Region, the salinity is at a maximum at the surface and decreases to a distinct minimum at about 500 meters depth. In spite of this salinity distribution the water column is stable due to the temperature structure (Dodimead et al., 1963). The salinity minimum of the Subtropic Region is the core of the Subarctic Intermediate water.

Favorite and Hanavan (1963) defined two fronts in the North Pacific: a temperature front associated with an almost vertical isotherm of 4°C, and a salinity front associated with the isohaline of 34.00%. They considered the area to the north of the temperature front to be the Subarctic Region, the area between the two fronts to be the Transition Region, and the area to the south of the salinity front to be the Subtropic Region. Subarctic waters are characterized by a temperature minimum and Subtropic waters by a salinity minimum at middle depths. But Transition waters do not have a temperature or salinity minimum. In the Western Pacific the fronts coincide and

form a sharp boundary, whereas in the Central Pacific they are about 300 miles apart.

Reid (1965) published a monograph entitled Intermediate Waters of the Pacific Ocean. He concluded that the Subarctic Intermediate Water does not originate at the sea surface, because the density surface that closely corresponds to the salinity minimum zone only occasionally intersects the sea surface in small areas off Kamchatka and the Kuril Islands. He pointed out that, even though the contact between the atmosphere and this density surface is limited, cooling, freshening and aeration are observed on it. He proposed that the characteristics of the Subarctic Intermediate Water are formed in high north latitudes by vertical mixing through the pycnocline. That is, vertical eddy conductivity and diffusivity without convective overturn to the depth of this density surface. According to him, this seems consonant with the known deep circulation of the Pacific Ocean which involves massive upwelling in the Subarctic Region rather than overturn to intermediate depths.

Dodimead et al. (1963) defined "domains" for the Subarctic Region. Applying the geostrophic method they studied the system of currents at the surface, 200-meter and 500-meter depths, with an assumption that a level of no motion exists at 1000-meter depth. However, they recognized that this level may be in appreciable motion in some parts of the region and recommended further studies on this problem.

McAlister, Favorite and Ingraham Jr. (unpublished manuscript) studied the influence of the Komandorskie Ridge on the surface and

deep circulation in the Northwestern Pacific Ocean. They stated that, although transport in deep waters may be significant, the dynamic topography provides a good representation of surface flow and that the direction of the subsurface flow to 2000 meters depth is generally the same as at the surface.

The surface circulation relative to 1000-meter depth in the extreme Western Pacific consists of the warm saline Kuroshio Current which moves northward along the Japanese Islands with the main flow turning eastward at about 36°N. This water continues eastward as the North Pacific Current to about 150°W where it moves southward. Part of the Kuroshio continues northeast to about 40°N where it meets the cold southward-moving less saline current, Oyashio, which is present along the eastern side of the Kuril and northern Japanese Islands. At the confluence of the two currents extensive mixing occurs both horizontally and vertically. These mixed waters continue eastward as the "West Wind Drift" with a slight northern component carrying it to about 45°N in the vicinity of 180°E. From there it continues eastward to approximately 300 miles from the Washington-Oregon coasts. Here the water divides -- part turns south to form the California Current, and a small part intrudes into the area off the coast of Vancouver Island and then moves southward along the coast; the remainder flows north into the Gulf of Alaska. The part of the Oyashio Current that does not actively mix with the Kuroshio Current moves northeastward to within 60 miles of the Aleutian Islands in the vicinity of 180°E. Most of this water moves east as the Subarctic Current. It

eventually flows into the Gulf of Alaska and around the Alaskan gyre, making its return in the strongly westward flowing Alaskan Stream along the southern side of the Aleutian Islands. The remainder of the water forms a gyre centered at about 50°N, 165°E. The water at the edge of the gyre mixes with the water of the Alaskan Stream, moves westward to the end of the Aleutian chain and then a portion of it enters the Bering Sea. While some of this water flows northward to the Arctic Ocean through the Bering Strait, the main branch forms a cyclonic circulation which flows southward along the Siberian coast. One part of this main branch becomes the East Kamchatka Current and the other is absorbed into the cyclonic gyre present in the central Bering Sea (Dodimead et al., 1963).

Favorite (1965) concluded that the Alaskan Stream is continuous as far westward as 170°E where it divides sending one branch into the Bering Sea and one southwestward to join the eastward flowing Subarctic Current at about 165°E.

According to McAlister et al. (unpublished manuscript) the Komandorskie Ridge marks the westernmost extent of the Alaskan Stream as a well-defined feature. The ridge appears to inhibit any deep circulation. However, it does not seem to have an effect on the Kurashio-Oyashio flow. They also indicated that in a north-south vertical section of temperature the deepening of the isotherms near the Aleutian Trench suggests that the Alaskan Stream extends to 4000 meters depth.

Although some studies have been accomplished in the North Pacific Ocean with reference to its chemical oceanography, much

needs to be done. Detailed rationalized studies of the overall patterns of vertical and horizontal distribution of physico-chemical parameters are far from being complete.

Trying to determine the direction of water motion between 1000-and 2000-meter depths in the Northeast Pacific Ocean, from the coast of America to 150°W and from 20°N to the north, Pytkowicz and Kester (1966) used apparent oxygen utilization (AOU) and preformed phosphate concentrations. Their results suggest a northward motion at low latitudes and southward motion at high latitudes with a divergence off the California coast.

Park (1967) studied chemical features in a section near 170°W, from 35°N to 50°N. In addition to the use of the isohaline structure of 34.0% to locate the Subarctic Boundary, he found other surface chemical parameters are also useful. Near the boundary, within a distance of one degree of latitude apart (60 miles) surface phosphate concentrations changed from 0.5 to 0.9  $\mu$ M, pH from 8.27 to 8.18, and the silicate concentration from 3 to 19  $\mu$ M. However, since these chemical boundaries were observed during summer, the same may not be true for other seasons of the year.

The surface distributions of phosphate and silicate from 35°N to the Aleutian chain and from 162°W to 180°W, had been studied in spring (Park, Hager, Pirson and Ball, 1968). Both silicate and phosphate were higher at the northern part with a maximum of 2.0µM phosphate and 30 µM silicate at 49°N, 173°W. They did not give a definite explanation of the mechanism responsible for this, mentioning the possibilities that the occurrence of phosphate and silicate

maxima may be either a product of the upward divergence of the subsurface water or that the high nutrient area has a very late production in April-May, or both phenomena coupled.

Anderson, Parsons and Stephens (1969) studied the nitrate distribution in the Subarctic Northeast Pacific Ocean and suggested that the maintenance of high nitrate concentrations over much of the area is due to the same factors that Park et al. (1968) mentioned.

In the book entitled "Chemistry of the Pacific Ocean," the members of the Institute of Oceanology of the U.S.S.R. Academy of Science discussed the distribution of temperature, salinity, oxygen and nutrients in the Subarctic Region. They included several graphs of these parameters showing the overall picture, both vertical and horizontal, at different locations and depths. pH and specific alkalinity are also shown and discussed for the overall patterns at different depths.

Sugiura (1965b) studied the distribution of reserved (preformed) phosphate in the surface waters of the Subarctic Pacific Region from about 45°N to the north and in the western part of the Bering Sea. He described a mechanism by which he believes the relatively high concentration of preformed phosphate is maintained in this region.

Kester and Pytkowicz (1968) examined the degree of oxygen saturation of surface waters in the Northeast Pacific Ocean, from about 20°N to the north and from the coast of North America to 180°W. They observed large differences between winter and summer conditions such as 97% in winter and 105% in summer for some parts of the Gulf of Alaska, and 101% in winter and 105% in summer for the

sea off Baja California. They related these differences to photosynthesis, warming of the surface waters, and upwelling.

To explain the distribution of the chemical parameters that are affected by the biological activity, it is very important to know how the organic primary productivity changes with the seasons of the year. Parsons, Giovando and LeBrasseur (1966) described the spring phytoplankton bloom in the Eastern Subarctic Region from estimations of the critical depth and the depth of the mixed layer. Their description was supported by the distribution of copepods in the region during April. Organic primary production data show values of up to 1100 mg  $C/m^2/day$  during the period May-June compared with values of 200 or less mg  $C/m^2/day$  during March-April, at Ocean Station "P" located at 50°N, 145°W (McAllister, 1962).

The purpose of this thesis is to clarify to some extent the mechanisms that are responsible for the distribution of the physicochemical parameters in the central North Pacific Ocean, giving special attention to the characteristics of the Subarctic Boundary and the salinity minimum zone of the Subtropical Water Mass. In trying to elucidate these mechanisms I have tried to give due importance to both the physical and biochemical processes for in Nature they are inseparable. An investigation of either one of them separately requires a high degree of arbitrariness, for although frequently one of them seems to be the most responsible process, the action of the other is always present. Thus, both create the actual chemicoceanographical structure of the water masses and their boundaries.

#### II. OBSERVATIONS

In 1968 a chemical-oceanographical group from Oregon State
University headed by P. Kilho Park participated in two cruises
aboard the USC&GSS Surveyor, the first in April-May and the second
in September-October. The positions of the hydrographic stations
from these cruises that were used in this work are shown in Fig. 1.

Detailed data from the first cruise were obtained for two sections. Determinations were made for temperature, salinity, dissolved oxygen, pH, alkalinity, nutrients and total carbon dioxide.

Data from the second cruise were obtained for five sections but only three or four stations per section had dissolved oxygen, pH, alkalinity and nutrients determinations.

pH was determined by a glass-electrode technique described by Park (1966). A Beckman pH meter, Model 7600, expanded scale, was used to measure the pH values. Dissolved oxygen and alkalinity were determined according to the manual of Strickland and Parsons (1965). Salinity was measured by a Hytech inductive salinometer manufactured by the Bissett-Berman Corporation, San Diego, California.

For plotting salinity, temperature, apparent oxygen utilization (AOU) and preformed phosphate on sigma-t surfaces, additional data were taken from YALOC 66 (Barstow, Gilbert, Park, Still and Wyatt, 1968) and Boreas (SIO reports, 1966) cruises. The location of the stations from these cruises that were used in this work is also shown in Fig. 1. For the YALOC 66 and the Boreas cruises the

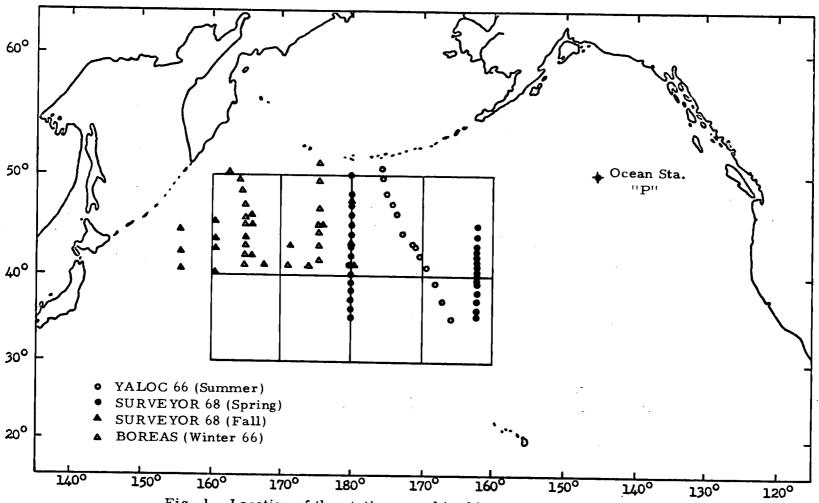


Fig. 1. Location of the stations used in this study, and Ocean Station "P".

procedures from the Strickland and Parsons' manual (1965) were also used to determine dissolved oxygen concentrations and inorganic phosphate. Salinity was determined by a Hytech inductive salinometer on Boreas cruise, and an inductive salinometer manufactured by Industria Manufacturing Engineers Pty. Ltd., Sydney, Australia, was used on YALOC 66.

#### III. RESULTS

#### Salinity

#### a) Vertical distribution

From the section along 162°W (Fig. 2), it can be seen that the Subarctic Boundary exists at 40°30'N, if we use the 34.0% vertical isohaline to define it. At 180°W (Fig. 3) the boundary was found at 44°N. At 180°W the isohaline of 34.0% is shown to be almost vertical from the surface to a depth of 200 meters. It tends to be horizontal in deeper waters and forms a tongue of irregular shape southward into the Subtropic Region as far as about 36°30'N. At 162°W the 34.0% isohaline is almost vertical from the surface to a depth near 250 meters. This isohaline then moves northward where it forms a tongue that extends to about 42°30'N. It then turns south to deeper waters.

A very distinct salinity minimum is shown in both sections—along 162°W it was found near 300 meters depth at 45°N and near 600 meters depth at 35°N; at 180°W the minimum clearly begins to appear near 45°N at a depth of about 200 meters and then irregularly increases in depth southward getting to 500 meters depth at 35°N. In general, the salinity minimum zone was found to be deeper at 162°W than at 180°W.

Between 600 and 1000 meters depth the isohalines show no general trend south of the boundary in both sections, but they gradually rise at the north as it has been observed in other studies.

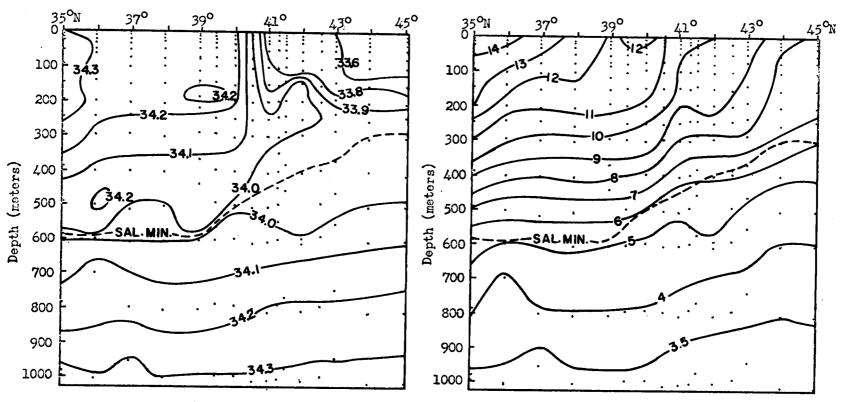


Fig. 2. Vertical distribution of S% (left) and  $T^{\circ}C$  (right) at  $162^{\circ}W$ .

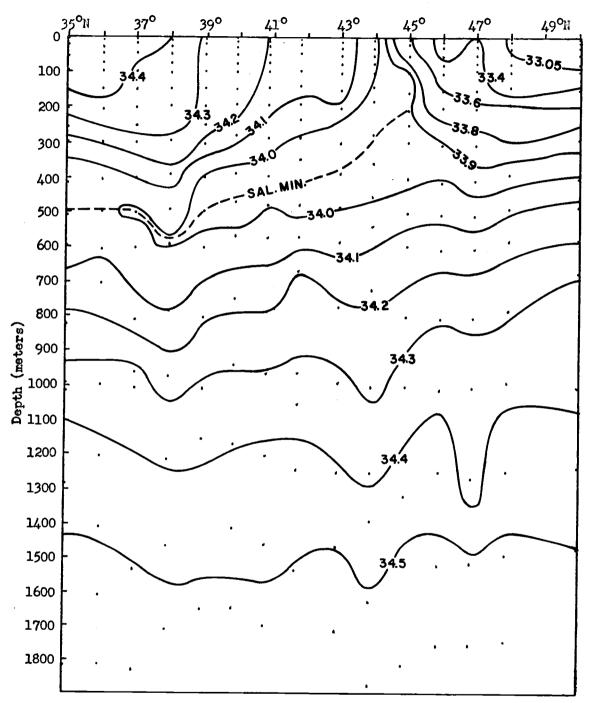


Fig. 3. Vertical distribution of S‰ at  $180\,^{\circ}W$ .

Below 1000 meters the isohalines show irregular distribution all the way from 35°N to 50°N at 180°W (Fig. 3).

b) Distribution on surfaces of sigma-t = 26.8 and sigma-t = 27.3

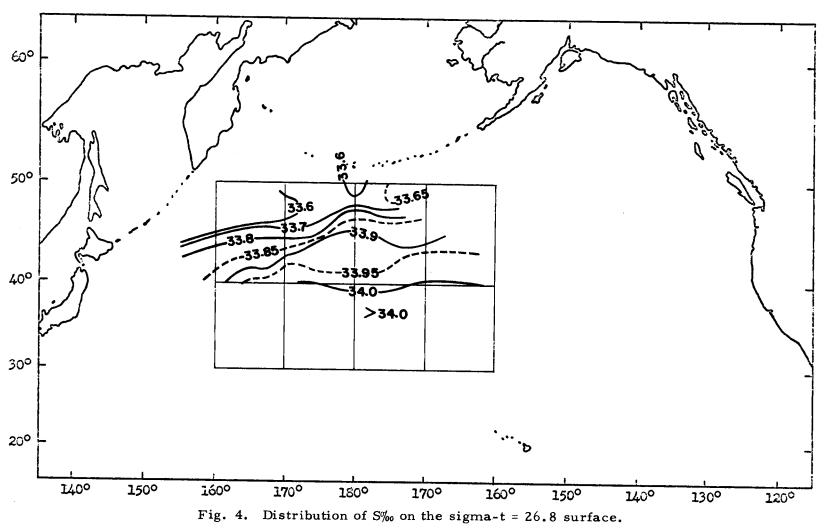
On the sigma-t surface of 26.8 (Fig. 4), the salinity is shown to vary with latitude from 34.0 % at about 40°N to 33.6 % at about 50°N. The variation with longitude is very small, decreasing slightly from east to west with exception of the northern part, from about 48°N to the north, where the change is irregular.

On the sigma-t surface of 27.3 (Fig. 5) the salinity changes slightly with latitude, from 34.3 % at about 40°N to a minimum of about 34.25 % and increasing again to 34.3 % in the northern part near 50°N.

#### Temperature

#### a) Vertical distribution

An almost vertical isotherm of 11°C, sinking from the surface to 200 meters depth, is shown at the boundary in the section along 162°W (Fig. 2), and another of 9°C from the surface to 100 meters depth is shown at the boundary in the section along 180°W (Fig. 6). In general the isotherms ascend from south to north—the farther north, the greater the slope. Along 180°W near 48°N, the 4°C isotherm is almost vertical from the surface to about 500 meters, which is the extreme case in the two sections. Along 180°W a temperature minimum was observed from 48°N to the north. This minimum existed at a depth of 300 meters at 48°N and at 200 meters



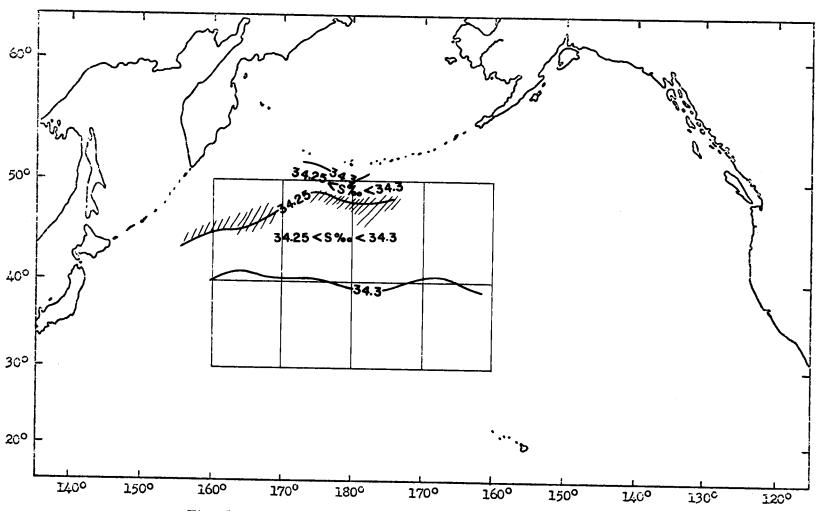


Fig. 5. Distribution of S% on the sigma-t = 27.3 surface.

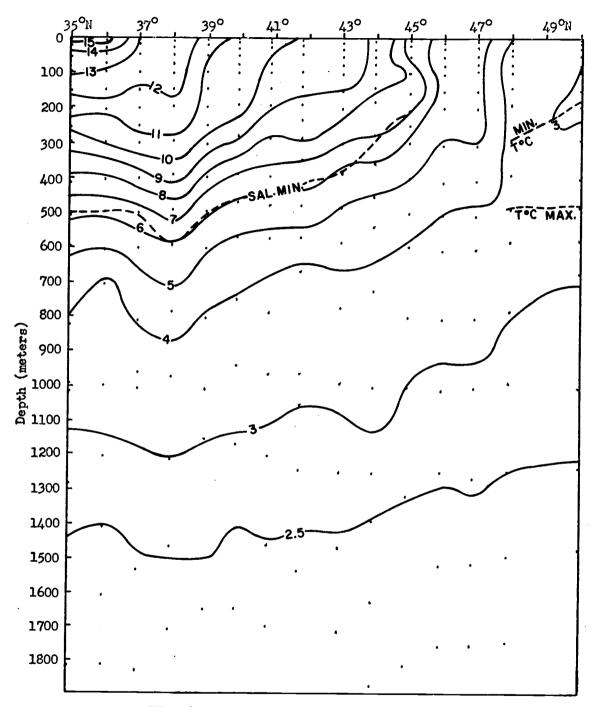


Fig. 6. Vertical distribution of T°C at 180°W.

at 50°N. Below this minimum, at approximately 500 meters, a temperature maximum was observed from 48°N to the north.

b) Distribution on surfaces of sigma-t = 26.8 and sigma-t = 27.3

On the sigma-t surface of 26.8 (Fig. 7) the temperature is shown to vary with latitude from 6.00°C at about 35°N to 3.00°C at about 50°N. The change with longitude is small and irregular.

On the sigma-t surface of 27.3 (Fig. 8) the temperature is shown to change slightly from 3.45°C at about 35°N to 3.30°C at about 50°N, passing through a minimum of 3.15°C near 48°N at 180°W.

#### Sigma-t distribution

The sigma-t isograms show in general a tendency to rise northward (Fig. 9 and 10). At the depth of the salinity minimum zone sigma-t is shown to vary within a range of 26.65 to 26.89 along 162°W, and within a range of 26.58 to 26.78 along 180°W.

#### Dissolved oxygen (oxyty)

Along 162°W (Fig. 9), at the south of the Subarctic Boundary, from the surface to a depth of 300 meters, the dissolved oxygen isograms are shown to slope downward as we go north but are horizontal north of the boundary. Below 300 meters, except for dome-like features at 36°N, 39°N and 43°N, the isograms are nearly horizontal south of the boundary but slope upward north of the boundary.

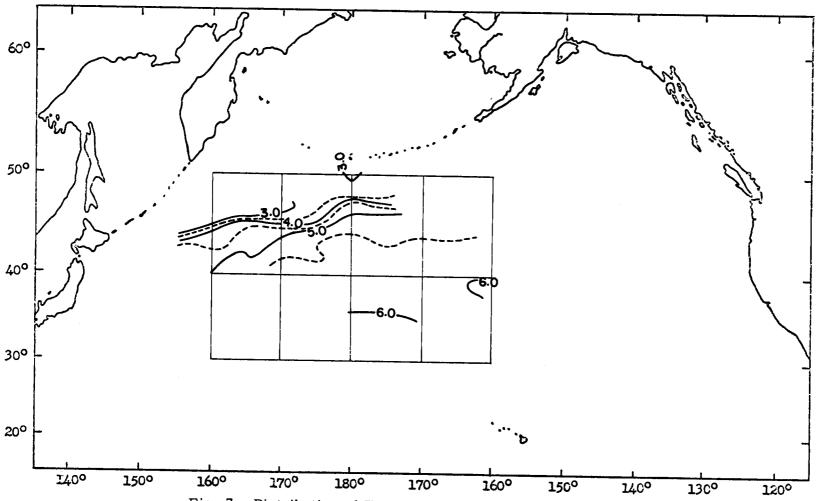
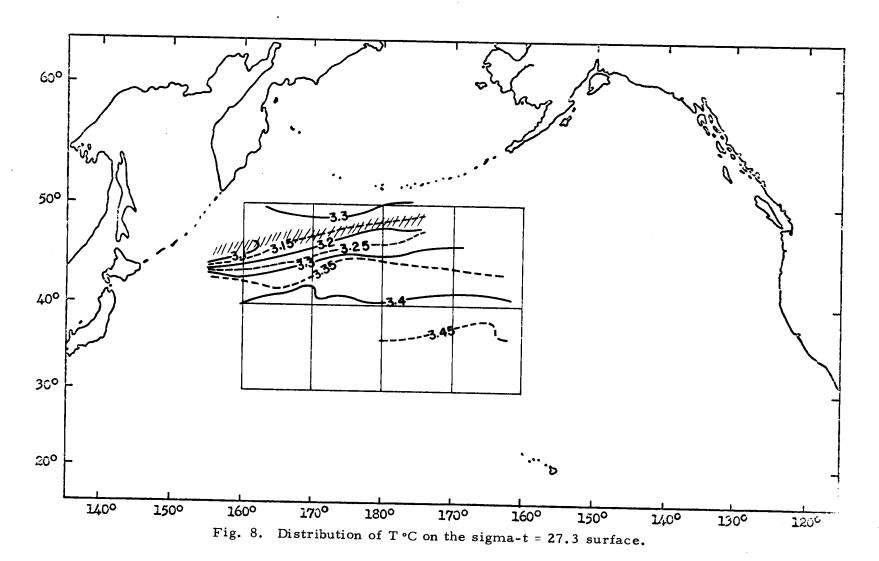


Fig. 7. Distribution of T°C on the sigma-t = 26.8 surface.



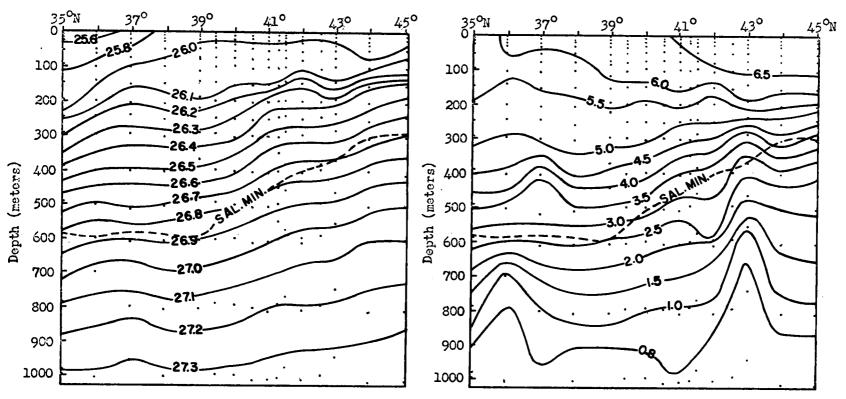


Fig. 9. Vertical distribution of sigma-t (left) and oxyty (right) at 162°W.

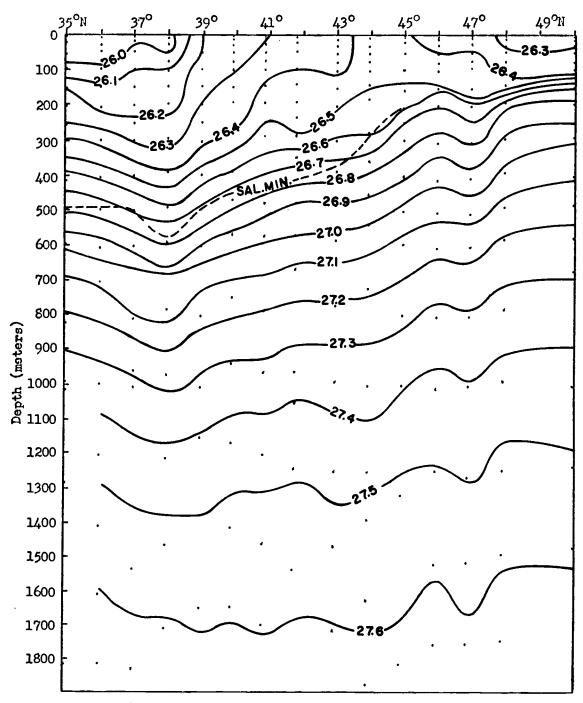


Fig. 10. Vertical distribution of sigma-t at  $180\,^{\circ}W$ .

Along 180°W (Fig. 11) from the surface to a depth of 400 meters, south of the boundary, the oxyty isograms are shown to slope downward to the north, and north of the boundary they slope downward to the south. Below 400-meter depth the isograms have a general tendency to slope upward to the north.

The dissolved oxygen minimum zone is present at a depth of 1100 meters at 35°N. Its depth increases as we go north, reaching 1250 meters at 44°N and then decreases to 700 meters at 50°N. The concentration of dissolved oxygen at the minimum zone varies from 0.65 ml/l at 35°N to 0.50 ml/l at 50°N.

#### pН

The isograms of pH show in general the tendency to slope upward to the north in both sections (Fig. 12 and 13).

In general the pH minimum zone was found at about the same depth as the dissolved oxygen minimum zone along 180°W (Fig. 13) except at the northern part, from 48°N to the north, where the pH minimum zone was found at shallower depths than the dissolved oxygen minimum zone. The pH was observed to vary at the minimum zone within a range of 7.76 to 7.79 without any noticeable variances.

The pH at the sea surface was very uniform; no sharp change of pH values was found at the surface to indicate the presence of the Subarctic Boundary. The difference between the extreme values at the surface was of the order of 0.06 pH unit.

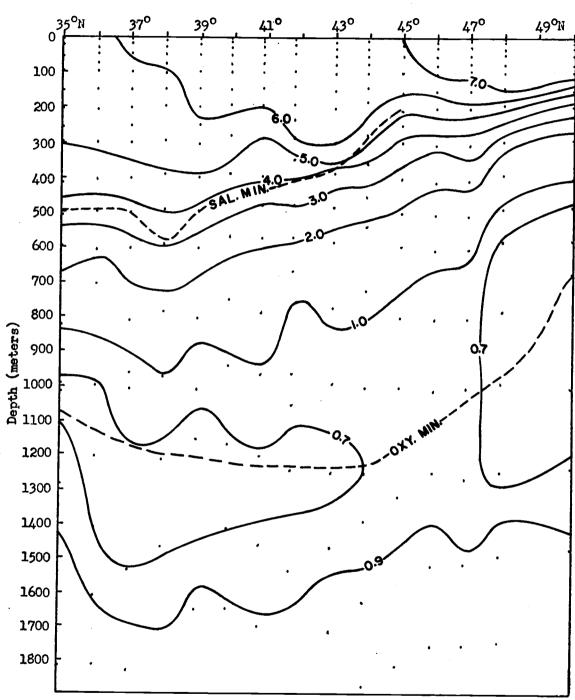


Fig. 11. Vertical distribution of oxyty at 180°W.

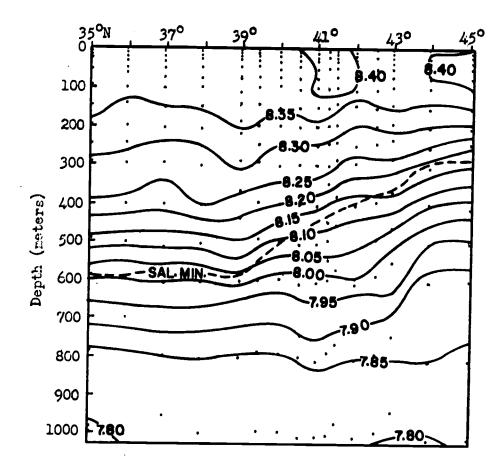


Fig. 12. Vertical distribution of pH at 162°W.

### Alkalinity

Along 162°W (Fig. 14) the alkalinity isograms are nearly horizontal south of the boundary. At the boundary they slope upward almost vertically, showing very clearly the difference between the Subtropic Region and the Subarctic Region. North of the boundary the isograms are shown to be nearly horizontal for some 2° latitude, from about 42°N to 44°N, and then they slope downward to the north.

Along 180°W (Fig. 15) the alkalinity isograms are very irregular, showing the general tendency to slope upward to the north.

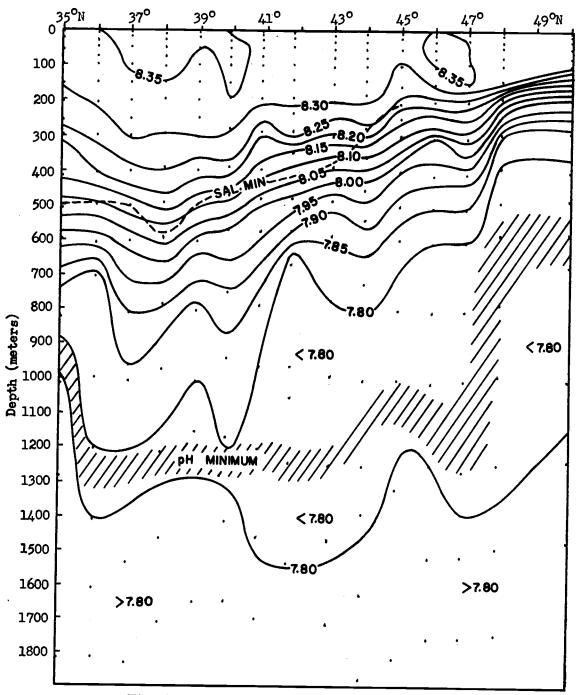


Fig. 13. Vertical distribution of pH at 180°W.

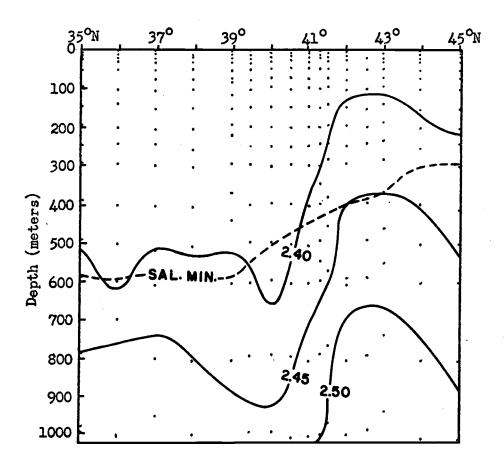


Fig. 14. Vertical distribution of alkalinity at 162°W.

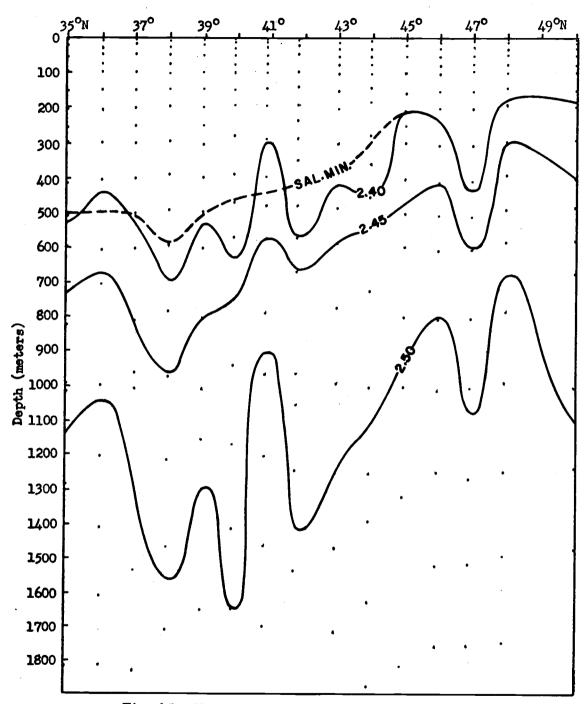


Fig. 15. Vertical distribution of alkalinity at 180°W.

## IV. DISCUSSION

## Salinity, temperature and sigma-t

Sverdrup et al. (1942), Dodimead et al. (1963) and Park (1966) observed that a temperature-salinity (T-S) diagram can clearly distinguish the Subarctic water mass from the Subtropical water mass (Fig. 16). Dodimead et al. (1963) discussed the principal features of the salinity and temperature structure of the Subarctic water mass (Fig. 17). The permanent features of the salinity structure are as follows: (1) an upper zone from 0 to about 100 meters depth; (2) a halocline in which the salinity increases by about 1‰ in the depth interval from about 100 to 200 meters; and (3) a lower zone in which the salinity increases gradually but

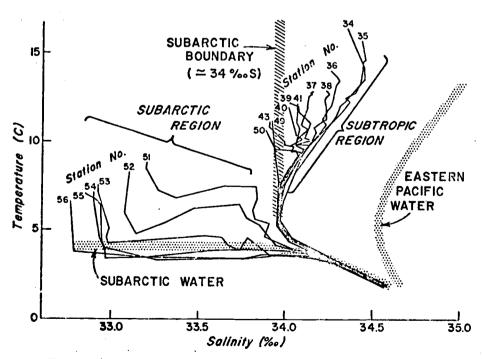
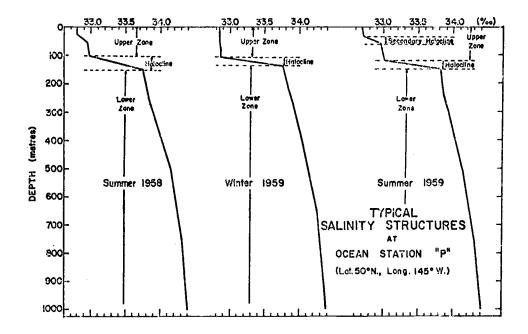


Fig. 16. Temperature-salinity (T-S) diagram for a series of stations across the Subarctic Boundary (after Park, 1966).



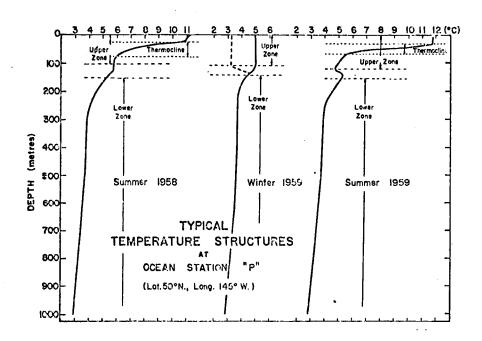


Fig. 17. Typical salinity (up) and temperature (down) structures at Ocean Station "P" (after Dodimead et al., 1963).

uniformly to about 34.4% at 1000-meter depth. Below this depth the salinity increases gradually to 34.67% at 5000 meters. The temperature structure has marked seasonal variations; the principal features of it are shown in Fig. 17.

Along 162°W and 180°W (Fig. 2 and 3) salinity shows a minimum which is the core of the so-called Subarctic Intermediate water. The farthest north where this minimum was observed was at 45°N (Fig. 3). It is attenuated to the south where it becomes the center of a tongue-like feature. This tongue of salinity could suggest a southward component of the direction of flow, but Sverdrup et al. (1942) mathematically proved that a tongue-like distribution of salinity in a vertical section can be either caused by horizontal and vertical mixing or by horizontal flow with vertical mixing. Therefore, tongues do not represent the axes of flow in every case.

Reid (1965) made a detailed review of the literature concerning the Subarctic Intermediate water and mentioned that several investigators (Koskliakov, 1961; Ichiye, 1954, 1956, 1962; Kuksa, 1962) have rejected the concept of southward transport of Intermediate Water by currents in the Western Pacific. In general, they agreed that the flow of the Intermediate Water is not markedly different from that of the surface waters and that both are part of a single winddriven system.

The section along 180°W (Fig. 6) shows a minimum and a maximum temperature strata from 48°N to the north. The minimum exists at 300-meter depth at 48°N, sloping upwards to 200 meters at 50°N. The maximum is located almost horizontally near 500-meter depth. They have been commonly referred to as Dicothermal and Mesothermal Water (Uda, 1935). The Dichothermal Water, which has also been called Inter-Cooled Water (Hirano, 1961), is formed in this region as a consequence of the seasonal cycle of heating and cooling (Uda, 1963). The warmer Mesothermal Water is not a direct result of the seasonal heating and cooling process since it occurs well within the lower zone; presumably it is associated with advection (Dodimead et al., 1963).

The Mesothermal Water was studied by Reid (1966) during the Boreas cruise. According to him, it is apparent that this warm subsurface water flowing westward with the Alaska Current does not come directly from the warm water of lower latitudes but comes from the Gulf of Alaska.

Hirano (1961) studied the distribution of salinity on the 26.75 sigma-t surface in the Northwestern Pacific near Japan and the Kamchatka Peninsula. He tried to correlate the Inter-Cooled Water with the Subarctic Intermediate Water, pointing out that an extension of the isogram of 26.75 sigma-t from the central part of the Inter-Cooled Water nearly coincides with the salinity minimum in the warm

water region at this part of the North Pacific Ocean. This type of correlation was not found at 180°W (Fig. 6), where the temperature minimum was observed at the sigma-t surface of 26.8 at 50°N, and at the sigma-t surface of 26.9 at 48°N. The salinity minimum for this section begins to appear at 45°N at the sigma-t surface of 26.6. It was found deeper southward crossing the 26.7 sigma-t surface at 44°30'N and occurred at the 26.8 sigma-t surface at 42°N. With this type of variation, it is difficult to get a reasonable relation between salinity minimum and temperature minimum observed. Hirano (1961) states that both water masses must have some thickness vertically containing the same sigma-t surface which in his case is sigma-t of 26.75 and in our case is sigma-t of 26.8. To make clear the relation between the Dichothermal and the Subarctic Intermediate waters, one must make a detailed study of the vertical structure of salinity, temperature and sigma-t to a depth of about 500 meters from 40°N to 50°N at different longitudes.

The temperature and salinity fronts (Fig. 2, 3, 6) have been studied by Favorite and Hanavan (1963) as possible indicators of limits for the environment of salmon. The temperature and salinity fronts show the location of the boundaries between Subarctic, Transition and Subtropic water masses. The temperature front, represented by the almost vertical isotherms of 4°C and 5°C, was located at about 47°-48°N (Fig. 6), about 3° farther north than the salinity front.

To study the distribution of physico-chemical properties in the salinity minimum zone and correlate it with the distribution at more northern latitudes, it was necessary to plot oceanographic parameters on properly chosen sigma-t surfaces. The distribution of conservative parameters on sigma-t surfaces, together with that of non-conservative parameters, may give useful indications about advective and mixing processes.

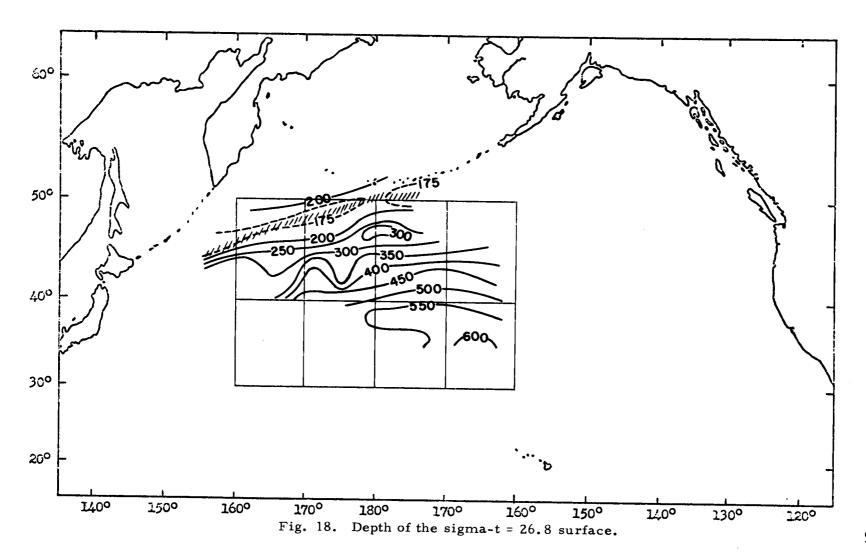
To do the plotting, data from the Surveyor 1968 Spring cruise and additional data from the Surveyor 1968 Fall cruise, YALOC 66 (summer) cruise (Barstow et al., 1968) and Boreas (winter 66) cruise (SIO reports, 1966) were used in an area between the latitudes 35°N and 52°N and the longitudes 162°W and 155°E.

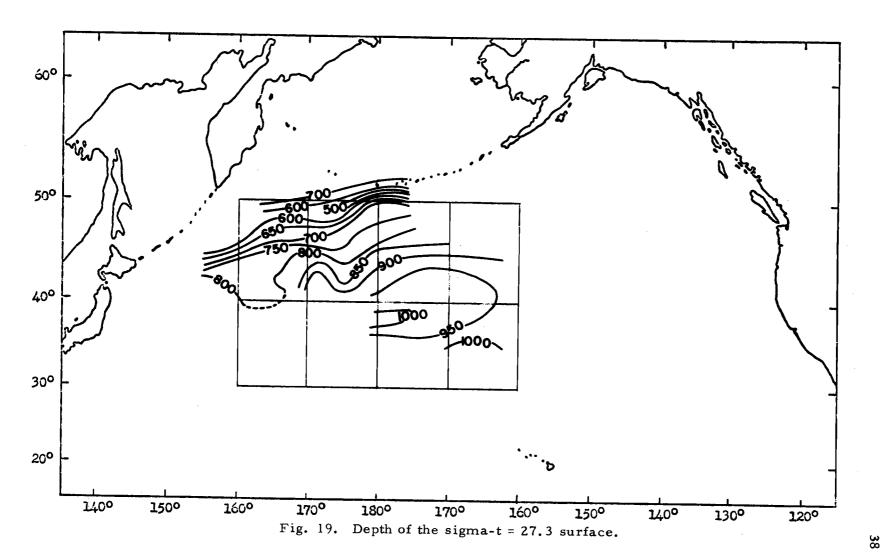
The sigma-t surface of 26.8 was chosen because it nearly coincides with the salinity minimum zone at these latitudes. At 162°W, sigma-t of 26.8 was observed to be approximately the mean value of sigma-t at the salinity minimum (Fig. 9). At 180°W this sigma-t value was found slightly below the salinity minimum (Fig. 10).

Depth, salinity, temperature, apparent oxygen utilization (AOU) and preformed phosphate were plotted on this sigma-t surface of 26.8. The same was done for the sigma-t surface of 27.3. The latter surface was chosen because it is close to 1000 meters depth which frequently has been assumed to be a level of no motion in applying the geostrophic method.

The topography of the 26.8 and 27.3 sigma-t surfaces (Fig. 18 and 19) is quite irregular, but there is a definite trend of decreasing depth from south to north to reach a minimum near 50°N and then it sinks farther north. In the Northern Hemisphere the current flows in such a direction that the water of low density is on the right-hand side of the current, and the water of high density is on the left-hand side (Sverdrup et al., 1942). In plotting the depth on the field of sigma-t, a minimum must then mark a division between two regions of opposite direction in currents. The topography of both sigma-t surfaces indicates a type of flow that, in general, is similar to that at the sea surface. However, in the southeastern part of our area of interest at sigma-t of 27.3, the topography shows a slight maximum at 38°N near 180°W.

The portion of the sigma-t surfaces having the shallowest depth has been called by Favorite (1969) the Ridge Area because of characteristic ridging in the subsurface salinity structure. It occurs near 50°N. To the north of this area lies the Alaskan Stream and to the south begins the general eastward flow. According to him, north-south flows across the Ridge Area can result in the formation of gyres which may fragment the circulation into two or more partially closed subsystems. Two commonly reported gyres are the Alaskan Gyre, usually centered south of the Alaskan Peninsula, and





the Western Subarctic Gyre, located near the western extremity of the Aleutian Islands.

The shallowest part of the sigma-t surface, being an area between two currents of opposite direction, is a zone where mixing, eddy conductivity and diffusivity is very likely to be strong. Reid (1965) proposed that aeration, cooling and freshening observed on the surfaces of thermosteric anomaly,  $\delta_t$ , equal to 125 cl/ton and 80 cl/ton, that correspond to sigma-t surfaces of 26.807 and 27.281, were caused by vertical mixing through the pycnocline. The increasing values of sigma-t with depth make a stratification that attenuates the vertical mixing. But it seems that, in spite of this, mixing is still capable of aerating water about 500 or more meters deep according to the vertical distribution of apparent oxygen utilization presented later in this work,

Tully and Barber (1960) estimated the upward flow of deeper water required to balance the net precipitation in the Gulf of Alaska. They assumed that the downward mixing of fresh water extends to the bottom of the halocline, which they located at about 200 meters. A calculated upward transport of  $20 \pm 10$  meters per year is necessary to maintain the average salinity of the upper 200 meters if the net annual precipitation in the region is 0.6 meters.

According to McAlister et al. (1970) these upwelled waters get into intermediate depths. The vertical distribution of certain

parameters show evidences that by some process of vertical mixing, perhaps eddy diffusivity, properties can be transferred from the sea surface to the deep waters and vice versa. This occurs especially in the area where the shallowest depth is observed on the sigma-t surfaces. Sugiura (1965b) tried to explain the mechanism responsible for the high concentration of reserved (preformed) phosphate in the oxygen minimum layer of the Subarctic Region by saying that the upper layer is the source of supply of reserved (preformed) phosphate for the oxygen minimum layer. In other words, the upper waters rich in reserved phosphate must be conveyed to the oxygen minimum layer through vertical mixing. The waters at the oxygen minimum layer rich in phosphate (both preformed and oxidative) must be transferred conversely to the surface through the same mechanism. Park et al. (1968) found the maximum concentrations of phosphate and silicate at the sea surface at 49°N, 173°W in the Ridge Area, and tried to explain it in terms of upwelling of deep waters.

The salinity and temperature distribution on the 26.8 sigma-t surface (Fig. 4 and 7) correlate well, with both decreasing from south to north. On the 27.3 sigma-t surface the salinity changes very slightly from south to north (Fig. 5), decreasing to a minimum which is a little farther south than the depth minimum and then increasing to the north. The temperature at the 27.3 sigma-t surface (Fig. 8) changes also slightly from south to north

decreasing to a minimum which nearly corresponds to the salinity minimum and then increasing to the north.

Favorite and Hanavan (1963) studied the surface distribution of salinity and found a broad minimum extending from 175°E eastward along the Aleutian Islands to 170°W and then southeastward to the coast of North America. This feature is not a noticeable permanent feature and, according to them, it could be a remnant of the previous summer's runoff from the Alaskan coast. There may be a relationship between the minimum of salinity at the 27.3 sigma-t surface and a minimum of salinity at the sea surface similar to that found by Favorite and Hanavan (1963). It could be that freshening and cooling by vertical mixing is stronger at the zone of the minimum salinity and temperature. More detailed studies of the salinity and temperature distribution at different sigma-t surfaces and at the sea surface using data from different seasons need to be done to clarify this.

In the northern part of the region, near 50°N, 180°W, the temperature is warmer at the 27.3 sigma-t surface than at the 26.8 sigma-t surface. This is due to the presence of the Dicothermal Water at the sigma-t of 26.8 and the Mesothermal Water at the sigma-t of 27.3. The difference in temperature between the two density surfaces is smaller than the difference between the temperature extrema because these sigma-t surfaces do not coincide

with the cores of these waters. Even though the temperature is warmer at the deeper sigma-t surface, the water column is stable due to the salinity structure.

Dissolved oxygen concentration (oxyty), apparent oxygen utilization (AOU), pH and preformed phosphate

Montgomery (1969) proposed the word oxyty for dissolved oxygen concentration. The apparent oxygen utilization (AOU) has been defined by Redfield (1942) as the amount of oxygen that has disappeared from the water owing to metabolic processes, and is calculated by subtracting the measured oxyty of the water parcel from the calculated amount of dissolved oxygen at saturation, assuming that it was in equilibrium with the atmosphere when it was at the sea surface.

It is well known that biochemical activity affects the pH and oxyty as well as the biogenous compounds. In the euphotic zone photosynthesis releases oxygen, increases the pH, and consumes carbon dioxide, phosphate, nitrate, nitrite, silicate and other micronutrients. Throughout the whole water column respiration consumes oxygen, liberates carbon dioxide and the micronutrients, thus lowering the pH.

Other physico-chemical processes affect pH and oxyty. Gas exchange at the sea surface, mixing, advection, inorganic oxidation and molecular diffusion affect the oxyty. Inorganic oxidation and molecular diffusion have a negligible effect on oxyty in the open ocean. Gas exchange at the sea surface, mixing, advection, the

change of temperature, of pressure with depth, and calcium carbonate dissolution or precipitation, affect the pH. The oxyty distribution with depth below the euphotic zone is basically determined by the process of decomposition of the organic matter and by advective and mixing processes.

Park (1968) studied, in a simplified model, the processes that contribute to the vertical distribution of pH in the northeastern Pacific Ocean. His conclusion was that the AOU effect is much greater than the dissolution effect of carbonate.

The pH was measured aboard the ship at 22°C and atmospheric pressure during the Surveyor 1968 Spring cruise. To obtain the "in situ" pH temperature and pressure corrections were made. The temperature corrections were made using Harvey's (1963) equation

$$pH_T = pH_{22 °C} - 0.0097(20-22) - 0.0105(T-20),$$
 (1)

where T is the "in situ" temperature in degrees centigrade. The pressure corrections were made using Culberson's (1968) values of  $K_{1p}^{i}$ ,  $K_{2p}^{i}$  and  $K_{Bp}^{i}$  in the equation

$$\frac{T_{(CO_2)}}{T_B} = \left[\frac{[TA]}{T_B} - \frac{K'_{Bp}}{a_{Hp}^{+K'_{Bp}}}\right] \left[\frac{(a_{Hp}^{-})^2 + a_{Hp}^{-K'_{1}} + K'_{1}^{-K'_{1}}}{a_{Hp}^{-K'_{1}} + 2K'_{1}^{-K'_{2}}}\right], \quad (2)$$

where  $T_{(CO_2)}$  is the total carbon dioxide present in all different

forms, that is,  $T_{(CO_2)} = [CO_2] + [H_2CO_3] + [HCO_3] + [CO_3]$ ,  $T_B$  is the total concentration of boron, [TA] is the total alkalinity,  $a_{Hp}$  is the hydrogen ion activity,  $K'_{Bp}$  is the apparent dissociation constant of boric acid and  $K'_{1p}$  and  $K'_{2p}$ , respectively, the first and second apparent dissociation constants of carbonic acid. The subscript p indicates pressure conditions.

Since  $T_{(CO_2)}$  does not change with pressure, it can be calculated using the  $a_{Hp}$  value, the Lyman's (1956) values of  $K_1'$ ,  $K_2'$  and  $K_1'$  at one atmosphere pressure and the "in situ" temperature. Knowing  $T_{(CO_2)}$  and using the Culberson's (1968) pressure coefficients to get  $K_1'$ ,  $K_2'$  and  $K_1'$  and  $K_2'$  at the "in situ" temperature and pressure, we can calculate the "in situ" hydrogen activity and, thus, the "in situ" pH. The effect of pressure is to decrease the pH.

The distribution of oxyty, apparent oxygen utilization and pH correlate well in both sections along 162°W and along 180°W (Fig. 9, 11, 20, 21, 12, and 13). Along 180°W the minima of pH and oxyty lie above the AOU maximum. The AOU isograms have the same general tendency to slope upwards from south to north. At the maximum the AOU values increase to the north from 6.8 ml/l at 35°N to 7.0 ml/l at 50°N.

Negative values of AOU near the surface indicate that the waters were supersaturated with oxygen. This supersaturation may be caused by photosynthesis or rapid warming of the surface layer, or

both. Data for concentration of chlorophyll or any other parameter indicating the organic primary production are needed to decide which factor was preferentially causing this supersaturation. In both sections supersaturation of oxygen was detected and negative values of AOU were found to 80-meter depth (Fig. 20 and 21). The vertical AOU distribution at 50°N, shown by data from one station of Surveyor 1968 Spring cruise, compared to that shown by one station of YALOC 66 (summer) cruise (Fig. 22), indicates that aeration by

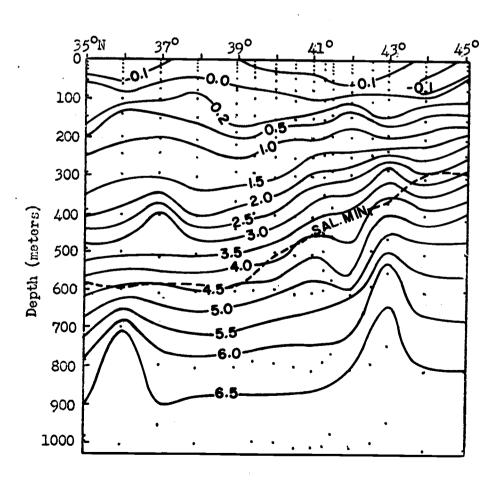


Fig. 20. Vertical distribution of AOU at 162°W.

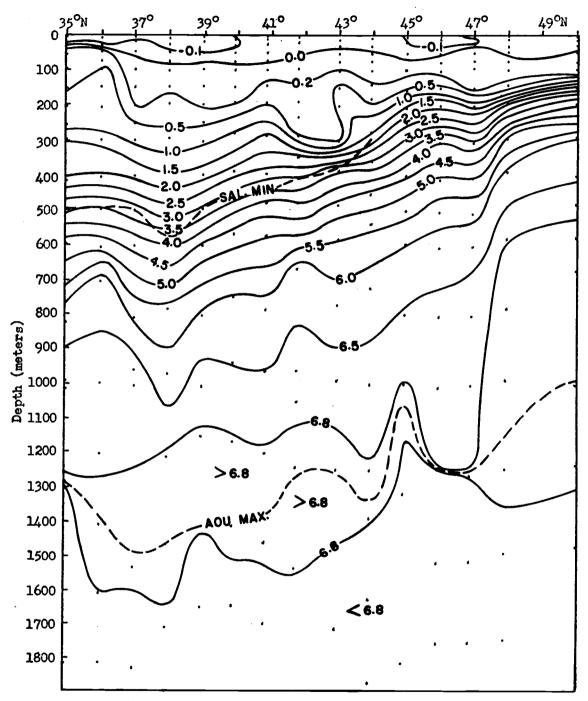


Fig. 21. Vertical distribution of AOU at 180°W.

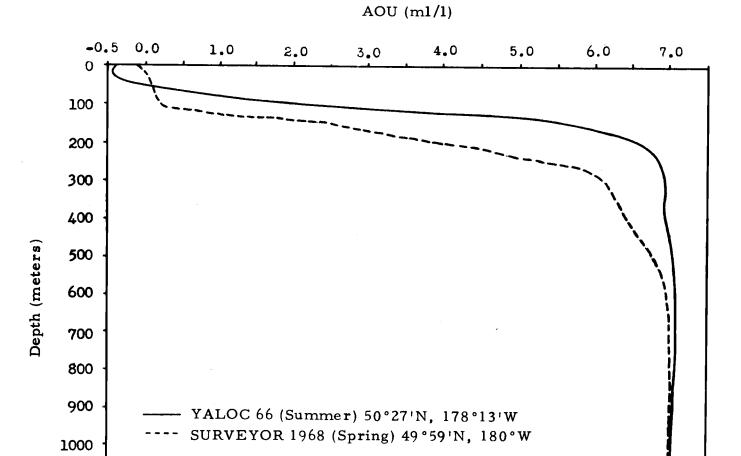


Fig. 22. Vertical distribution of AOU at one station of Surveyor 1968 Spring cruise and one of YALOC 66 (summer) cruise.

mixing, eddy diffusivity and conductivity takes place to more than 500 meters depth. In summer when photosynthesis is going on at a greater rate, AOU is higher than during spring at intermediate depths. After summer ends organic matter ceases to sink at a relatively high rate and mixing increases the oxygen content.

There has been some controversy about the usefulness of the AOU concept. Pytkowicz and Kester (1966) suggested that AOU values only approximate the actual oxygen utilization because the saturation value does not vary linearly with the temperature and salinity during mixing of waters at any depth. Also, because there may not be equilibrium with the atmosphere while waters are at the surface. But they mentioned that the non-linearity difference for the temperature and salinity gradients that one usually encounters on sigma-t surfaces is within the precision of oxyty determinations and, thus, it is negligible.

Therefore, according to them, we can use the AOU values to study the direction of motion. Increasing AOU values indicate the direction, in the sense of going from younger to older waters that have undergone more biological oxidation since leaving the surface, but not providing a distinction between advective and mixing processes. They pointed out that differences in surface productivity may cause different rates of oxidation at any particular depth, and if so these

differences have to be taken into account in the interpretation of AOU gradients.

To make the assumption that greater AOU means "older" water, we also have to assume that the increase in AOU is due to oxidation of organic matter, to a certain extent, and not just to mixing.

Menzel and Ryther (1968), after studying a section in the South Atlantic Ocean from 8°S to 37°S for oxyty and particulate and dissolved organic carbon, concluded that both dissolved and particulate organic matter below the immediate surface are nearly resistant to decomposition. They also concluded that, if there is respiration and decomposition going on below a depth of about 400 meters, these processes do not appear to have a measurable effect on the concentration of oxygen and dissolved organic carbon. They said that the oxyty and dissolved organic carbon concentration are governed by mixing between water masses. They were able to get good agreement between predicted and measured values of oxyty by using the "core" method of Wüst (1935) for prediction and tried to invalidate the usefulness of AOU in studying the direction of flow of water masses. On the basis of their conclusion, it is not possible to explain why and how differences in subsurface concentrations of dissolved organic carbon are produced and maintained in the Indian Ocean. The ranges they show for variability in dissolved organic carbon below 400 meters

are as large as 0.2 mgC/l which, in the extreme case, could account for an equivalent of about 0.5 ml/l of AOU.

To distinguish between advective and mixing processes we have to use conservative parameters such as salinity, temperature or preformed phosphate. Preformed phosphate was defined by Redfield (1942) as the phosphate that was present in the parcel of water before it left the sea surface, while oxidative phosphate is that which is released by biological oxidation. Preformed phosphate is conservative in the same sense in which temperature and salinity are conservative (Pytkowicz, 1968b), that is, it can be gained or lost only at the boundaries.

Pytkowicz (1968b), in studying the water masses and their properties at 160°W in the southern Pacific Ocean, was able to calculate the difference in AOU due to mixing between the Pacific Intermediate Water and the Pacific Deep Water. He calculated the fractions of these waters that were mixed by using the salinity values at the cores. Then, by subtracting the change in AOU due to mixing from the total change in AOU, he obtained the AOU change due to biological oxidation.

Different water masses have generally been found to have different preformed phosphate concentrations. Therefore, when mixing occurs between two water masses of different origin, we may observe a gradient of preformed phosphate, like the one found by

Redfield (1942) in the South Atlantic. The absence of a gradient of preformed phosphate suggests that advection is the only process occurring. This applies only for qualitative purposes; when there is some mixing we have to use more precise parameters, such as salinity, to calculate its extent. Pytkowicz and Kester (1966) expressed that, according to their experience, preformed phosphate is good to a  $\pm$  10% error.

Using the phosphate data from Boreas cruise and YALOC 66 cruise, preformed phosphate values were calculated for the sigma-t surfaces of 26.8 and 27.3, and plotted against latitude (Fig. 23).

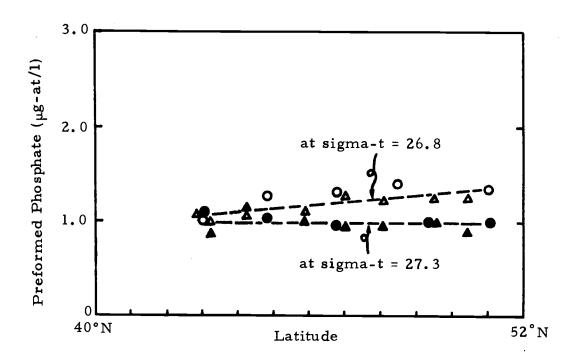


Fig. 23. Preformed phosphate distribution with latitude on the sigma-t = 26.8 and sigma-t = 27.3 surfaces from YALOC 66 cruise (Barstow et al., 1968) and Boreas cruise (SIO reports, 1966).

The section from YALOC 66 is near 170°W and that of Boreas is near 175°E. The results suggest that at the sigma-t surface of 27.3 there is no detectable mixing at these latitudes, with no appreciable change of preformed phosphate with latitude nor with longitude. At the 26.8 sigma-t surface there is no appreciable change of preformed phosphate with longitude, but there is an increasing trend northward. This observation indicates that there is only advection in the west-east direction while mixing is also occurring in the north-south direction at this density surface.

When there is no appreciable mixing among different water masses and the conditions in the euphotic zone with respect to organic primary production are the same throughout the area of study, the increase in AOU can be taken as increase in biological oxidation.

Under these conditions the distribution of AOU on the field of sigma-t must indicate a direction of flow similar to the real direction of flow. On the other hand, when there are mixing processes occurring and the organic primary production is likely to be different from place to place but the patterns of flow are already satisfactorily known by means such as geopotential topography, then the distribution of AOU compared to the geopotential topography may give indications of the type of mixing processes and the state of photosynthesis at the euphotic zone.

We are not able to do the type of calculations that Pytkowicz (1968b) did to know the extent of mixing because we are not dealing with mixing between two water masses with well-defined cores. The "core" method of Wüst (1935) as used by Menzel and Ryther (1968) is not applicable because we do not have a salinity core at the northern part of our area of interest, and it gives only qualitative indications not quantitative results.

When the motion is slow, the biological oxidation has more time to proceed for the same displacement in space than when the motion is fast. Therefore, if the oxidation rate is the same, the slower the motion the closer the AOU isograms are in space; the faster the motion the farther they are apart. It is not possible to get an indication of the relative magnitudes of velocity at different sigma-t surfaces based on the distribution of AOU because the rate of biological oxidation may change as a function of depth.

To plot AOU on the 26.8 sigma-t surface (Fig. 24) the data from the YALOC 66 cruise were not used because they were consistently higher than the data from both sections of the Surveyor 1968 Spring cruise which lie at both sides of that of YALOC 66 cruise (Fig. 1). These higher values may be due to the fact that YALOC 66 cruise was during summer when the primary productivity is relatively high at the surface waters of this region. This higher productivity causes more organic matter to sink below the euphotic zone

and, therefore, results in more biological oxidation. Park, Curl and Glooschenko (1967) reported surface concentrations of chlorophyll higher than 1 mg/m<sup>3</sup> during YALOC 66 cruise. Differences in AOU were greater near 50°N where the AOU reached a value of 5.8 ml/l during YALOC 66 cruise and less than 4.0 ml/l during Surveyor 1968 Spring cruise. Some of the stations from the Surveyor 1968 Fall cruise are very close in position to some of those from the Surveyor 1968 Spring and Boreas cruises (Fig. 1). For these stations the differences in AOU values from different cruises were less than 0.1 ml/l, which is in good agreement for our purpose, and indicates that the conditions with respect to primary production were similar during these cruises or that changes between fall, winter and spring do not have an appreciable effect on the distribution of AOU on the 26.8 sigma-t surface.

In plotting AOU's on the 27.3 sigma-t surface (Fig. 25)

YALOC 66 data was used together with the data from the other

cruises. The distribution of AOU on this density surface is

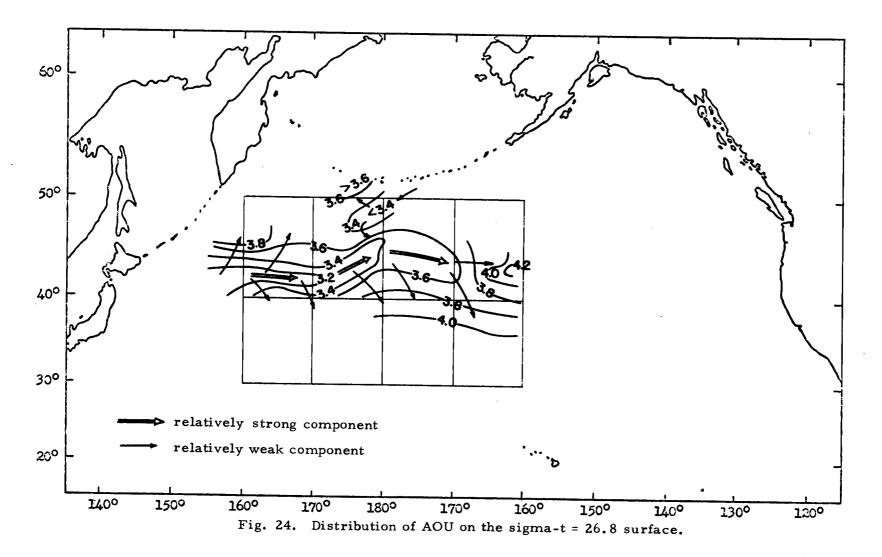
essentially the same with or without using YALOC 66 data. This

indicates that the effect of seasonal changes on the concentration of

chemical parameters at this sigma-t surface is very small compared

with that at the 26.8 sigma-t surface.

Acceleration potential contours, parallel to which the geostrophic flow occurs, were drawn by Reid (1965) on the surface



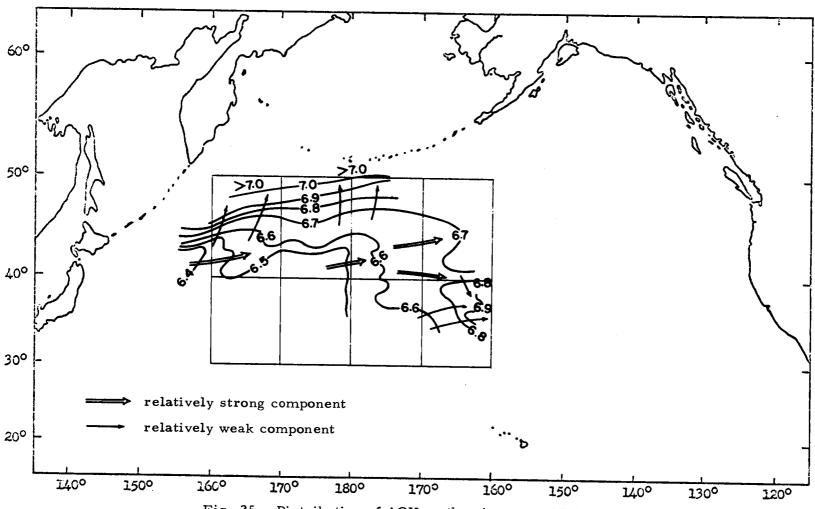


Fig. 25. Distribution of AOU on the sigma-t = 27.3 surface.

of  $\delta_t$  = 125 cl/ton and  $\delta_t$  = 80 cl/ton (Fig. 26 and 27). These values of thermosteric anomaly correspond to sigma-t values of 26.807 and 27.281 respectively. The patterns of flow of these sigma-t surfaces must be the same as those of the sigma-t surfaces of 26.8 and 27.3 because they almost coincide. The acceleration potential was calculated with respect to 1000 meters depth for the  $\delta_t$  = 125 cl/ton surface and with respect to 2000 meters depth for the  $\delta_t$  = 80 cl/ton surface. The figures are reproduced here to compare the geostrophic flow with the AOU distribution. On figures 24 and 25 the direction of flow suggested by the AOU distribution is indicated by arrows.

The direction of flow suggested by the AOU distribution on the 26.8 sigma-t surface agrees with that indicated by the geostrophic method (Fig. 24 and 26) except in two cases. Farther south than about 42°N AOU distribution indicates a relatively small southward component of flow that is not indicated by the acceleration potential. This could be caused by a gradient of organic primary production at the sea surface of this southern region with higher production at lower latitudes, causing more organic matter to sink down and consume oxygen at intermediate depths. Also, it could be caused by mixing of deeper water, with higher AOU, with waters at this density surface. To confirm the former explanation primary productivity data is needed. A better indication of what is going on could be given by plotting

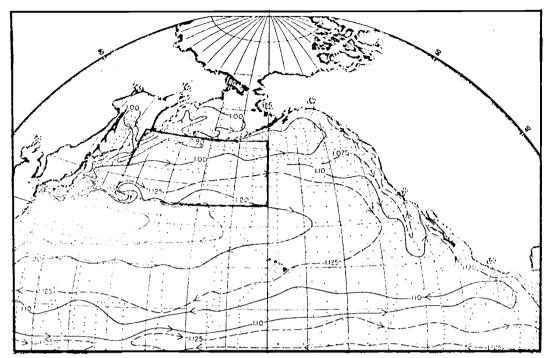


Fig. 26. Acceleration potential on the surface where  $f_t$  = 125 cl/ton (after Reid, 1965).

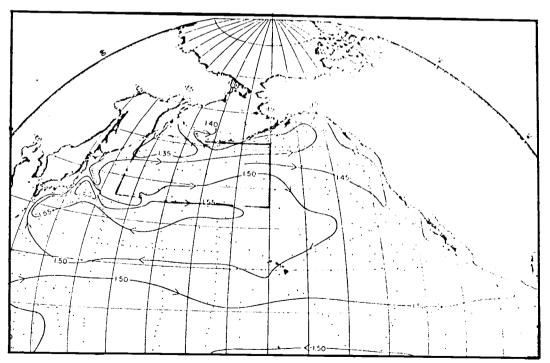


Fig. 27. Acceleration potential on the surface where  $d_t = 80 \text{ cl/ton}$  (after Reid, 1965).

AOU distribution on this density surface for different seasons, mainly winter and summer, and comparing the results with the surface distribution of chlorophyll concentration or some other parameter indicative of the organic production. At the northern part, between 175°E and 180°W, AOU distribution indicates a linkage between the westward flow south of the Aleutian chain and the eastward flow farther south. This linkage is not indicated by the acceleration potential. The reason for this may be that the flow is slow and not well enough defined to be detected and measured by the geostrophic method.

Favorite (1965) says that the Alaskan Stream divides at 170°E, sending one branch into the Bering Sea and one southwestward which joins the eastward flowing Subarctic Current. If the pattern of flow at the 26.8 sigma-t surface, which at these latitudes is at about 200 meters depth, is similar to that at the sea surface, the flow suggested by the AOU distribution is real and there is a linkage between the westward and the eastward flow on this density surface.

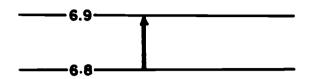
The tongue of low AOU near the Aleutian chain also gives an indication of vertical mixing. If there would be no mixing, the waters would continuously lose oxygen by biological oxidation when flowing around the Alaskan Gyre and along the Aleutian chain; therefore, there would be higher AOU values near the Aleutian chain, in the region of westward flow, than farther south in the region of eastward flow. Because this is not the case, then, the water at 26.8 sigma-t

surface has been aerated by vertical mixing, mainly at the depth minimum, near 50°N, with later reduction of oxygen content by biological oxidation while flowing southwestward to join the eastward flowing water.

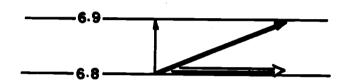
The direction of flow suggested by the AOU distribution on the 27.3 sigma-t surface agrees with that indicated by the geostrophic method (Fig. 25 and 27) with the exception that the westward flow near the Aleutian chain is not indicated by the AOU distribution.

This may be due to the fact that the oxygen minimum zone is at this density surface at 50°N (Fig. 26). The oxygen concentration is so low, 0.5 ml/l, that further oxidation decreases the oxygen concentration by a very small amount and there is no appreciable gradient of AOU with change of longitude to detect the flow south of the Aleutian chain.

By comparing the AOU distribution at the 27.3 sigma-t surface and the acceleration potential contours of the  $\theta_t$  = 80 cl/ton surface (Fig. 26 and 27) one realizes that it is easy to misinterpret the AOU distribution when only analyzing a small part of the picture. For example, when we consider the small square between 170°E and 180°W, and 45°N and 50°N (Fig. 25), the water flow appears to be perpendicular to the AOU isograms (Fig. 28), directed almost completely to the north, when actually only a small component of the direction of flow is towards the north with the main component being



Inferred direction of motion with only one component to the north



Actual direction of motion with the main component to the east

Fig. 28. Two AOU isograms with the "suggested" and actual direction of flow indicated by arrows.

towards the east. This indicates that whenever one is going to interpret the AOU distribution on sigma-t surfaces, broad pictures covering a big area are needed to determine the direction of flow from the overall pattern.

## Alkalinity and specific alkalinity

Specific alkalinity has been defined as the ratio of alkalinity to chlorinity. It does not vary with addition or removal of fresh water or carbon dioxide to or from seawater, but it changes with calcium

carbonate precipitation and dissolution occurring in seawater (Park, 1966).

The vertical distribution of alkalinity at 162°W (Fig. 14) shows very clearly the presence of the Subarctic Boundary at about 41°N where the isograms are almost vertical. Because the waters to the north of the Subarctic Boundary have a lower salinity than those to the south, with respect to the same depth, specific alkalinity shows the presence of the boundary more clearly than alkalinity (Fig. 29).

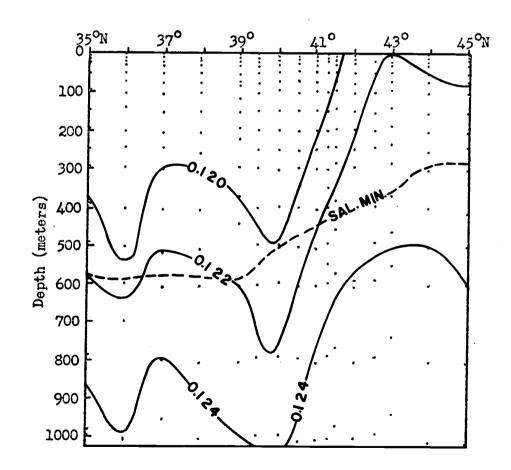


Fig. 29. Vertical distribution of specific alkalinity at 162°W.

Along 180°W the distribution of both alkalinity and specific alkalinity (Fig. 15 and 30) do not show clearly the presence of the boundary. They show the general trend for the isograms to slope upwards from south to north.

## Percent saturation of calcium carbonate with respect to calcite

Measurements of pH, total alkalinity, temperature, salinity and depth can be used for the calculation of the "in situ" percent saturation of calcium carbonate. The percent saturation of calcium carbonate in a solution is expressed as the ratio of the ionic product of calcium and carbonate to the equilibrium solubility product of calcium carbonate, multiplied by one hundred, i.e.,

$$\%S = \frac{[Ca^{++}] \cdot [CO_3^{=}]}{K'_{SPp}} \times 100$$
 (3)

where [Ca<sup>++</sup>] and [CO<sub>3</sub><sup>=</sup>]<sub>p</sub> are the total concentration of calcium and carbonate ions, respectively, including both free ion and ion-pair forms, and K'<sub>SPp</sub> is the apparent solubility product of calcium carbonate. The subscript p indicates pressure conditions.

The use of apparent constants is preferred to the use of thermodynamic constants since it eliminates the need to know the extent of ion-pair formation in seawater (Hawley and Pytkowicz, 1969).

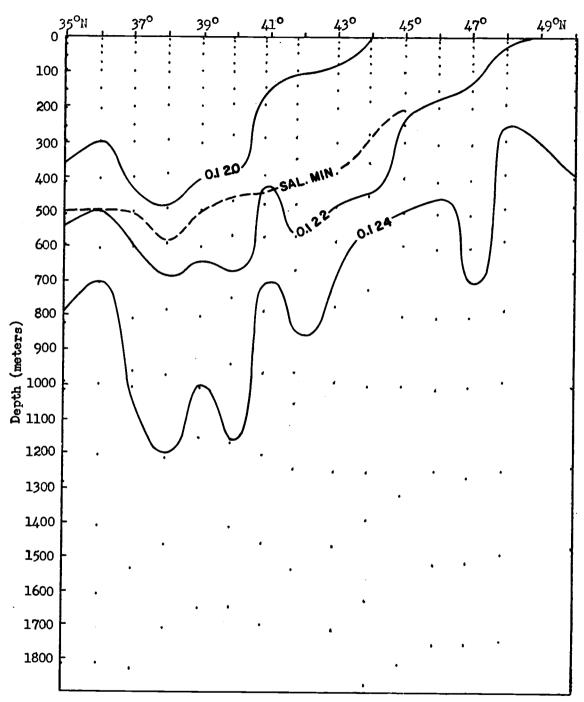


Fig. 30. Vertical distribution of specific alkalinity at 180°W.

A practical choice of K'SPp is that of reasonably pure calcite because it represents a lower limit for the range of solubility of calcium carbonates, and may be used to set the deepest limit for supersaturation in the oceans (Pytkowicz, 1968a).

To calculate the total concentration of calcium, [Ca<sup>++</sup>], the Wattenberg's (1936) relationship was used:

$$[CA^{++}] = 1/2[CA] + 477 \times 10^{-6} Cl\% \text{ (moles/liter)}$$
 (4)

where [CA] is the carbonate alkalinity calculated from the expression:

$$[CA] = [TA] - \frac{T_B \circ K'_{Bp}}{K'_{Bp} + a_{Hp}}$$
(5)

The total concentration of boron, TB, was calculated from the expression:

$$T_B = 2.2 \times 10^{-5} \text{Cl}\% \text{ (moles/liter)}$$
 (6)

To calculate a "in situ" values of pH were used.

To calculate the total concentration of carbonate ion at pressure P,  $[CO_3^{=}]_p$ , the expression:

$$[CO_3^{=}]_p = [CA] \left[ \frac{K_{2p}'}{a_{Hp} + 2K_{2p}'} \right]$$
 (7)

was used.

The equations derived by Li, Takahashi and Broecker (1969), using Lyman's (1956) values, were used to calculate the apparent dissociation constants of boric and carbonic acid at one atmosphere

pressure, and the equations of Culberson (1968) were used in the calculations of the pressure coefficients of these constants.

Li, Takahashi and Broecker (1969), using the values of the apparent solubility product of calcium carbonate that MacIntyre (1965) measured for calcite over a temperature range of 0° to 40°C and estimating the effect of chlorinity on the basis of measurements by Wattenberg (1936), derived an equation for K'SP which is the apparent solubility product at one atmosphere,

 $K'_{SP} = (0.69 - 0.0063T_1 \times 10^{-6}) \cdot (Cl\%/19) \text{ moles}^2/\text{liter}^2$  (8) where  $T_1$  is the ''in situ'' temperature in degrees centigrade.

Knowing  $K'_{SP}$  we can calculate  $K'_{SPp}$  applying a pressure coefficient:

$$\frac{K_{SPp}^{\prime}}{K_{SP}^{\prime}} = 10^{-\Delta V \cdot Z/23RT} 2$$
 (9)

where  $\Delta V$  is the change in partial molar volume for calcium carbonate for the reaction of dissociation in seawater, Z is the depth in meters, R is the gas constant and  $T_2$  is the absolute "in situ" temperature.

Values of  $\Delta \overline{V}$  are available in the literature only for temperatures of 25°C, 22°C and 2°C. Hawley and Pytkowicz (1969) calculated the pressure coefficient of  $K_{SP}^{!}$  for aragonite at 2°C and, by assuming the temperature dependence of calcite to be the same as that of aragonite, they calculated the values of the pressure

coefficient of  $K'_{SP}$  for calcite at 2°C and 500 and 1000 atmospheres. Using those values in the equation for the pressure coefficient of  $K'_{SP}$   $\Delta V$  was found to be equal to -35.8 cubic centimeters per mole at 2°C (Hawley, personal communication).

The temperatures are higher than 5°C only in the upper 600 meters at the southern part of both sections, along 162°W and 180°W, being lower than 5°C in deeper and farther north waters (Fig. 2 and 6). The effect of pressure on the apparent solubility product is small down to 600 meters depth. Due to this I used the value of  $\Delta V$  for 2°C as a constant in the calculations of the pressure coefficient of  $K_{SP}^{I}$ . The error due to this is negligible.

The vertical distribution of the percent calcium carbonate saturation with respect to calcite along 180°W and 162°W shows the general trend for the isograms to slope upwards from south to north (Fig. 31 and 32). This corresponds closely to the distribution of sigma-t. This indicates that the distribution of the percent saturation is mainly governed by flowing and mixing along sigma-t surfaces in this region.

The surface waters are more supersaturated with calcium carbonate at the southern part of our sections than at the northern part; this difference is due to the higher temperatures at the south. In the surface waters, at 180°W, the percent saturation is more than 400% at 35°N and between 250-300% at 50°N.

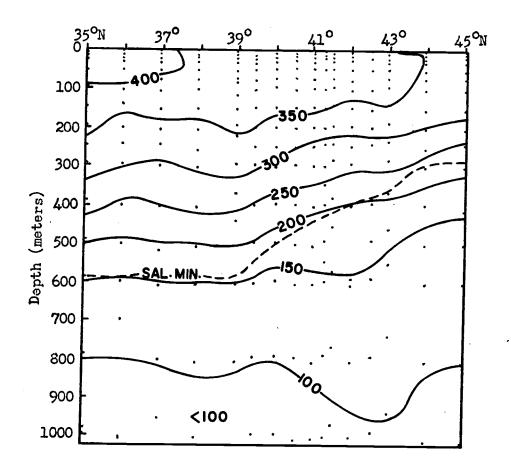


Fig. 31. Vertical distribution of the percent saturation of calcium carbonate with respect to calcite at 162°W.

In both sections, along 162°W and 180°W, at 35°N the waters appear to be supersaturated from the surface to a depth of about 800 meters and undersaturated from 800 to 1800-2000 meters depth. At 50°N (Fig. 31) undersaturation was observed to begin from a depth of about 400 meters.

A minimum zone of the percent saturation is shown at about 1000-1500 meters depth. This correlates with the pH minimum and the AOU maximum zones (Fig. 13, 21 and 32).

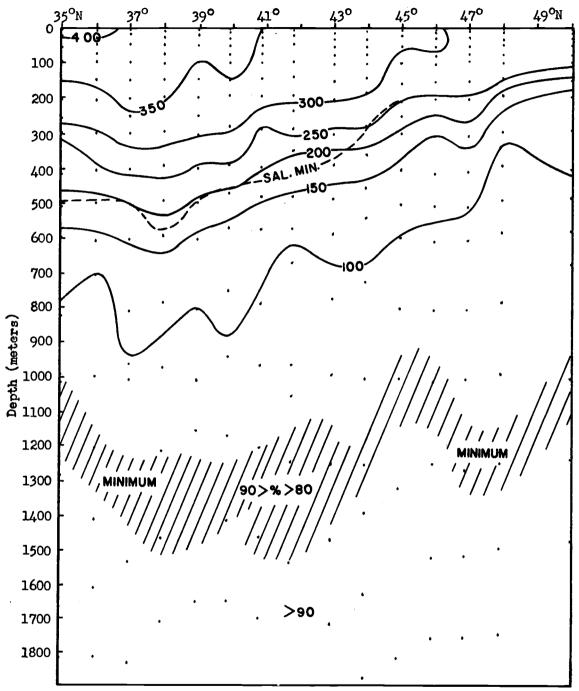


Fig. 32. Vertical distribution of the percent saturation of calcium carbonate with respect to calcite at 180°W.

To look at the correlation of pH, AOU and the percent saturation of calcium carbonate with respect to calcite, their values were plotted against depth (Fig. 33, 34, 35) for four deep stations of the Surveyor 1968 Spring cruise, which positions are shown in the figures. It is clearly seen that, except for the values near the sea surface, when the AOU is high, the pH and the percent saturation are low. From about 2000 meters to 5000 meters depth, the waters are saturated or slightly oversaturated. This corresponds to the deep pH maximum. Below 5000 meters depth the waters are undersaturated due to the increasing effect of pressure on the solubility product of calcium carbonate and on the pH.

The vertical distribution of percent calcium carbonate saturation shown in Fig. 32 disagree, with respect to the absolute values, with that found by Hawley and Pytkowicz (1969) using data from a station of YALOC 66 cruise (Barstow et al., 1968) at 176°13.8'W, 50°27.5'N. But the general trend of the distribution is quite similar with a minimum of saturation at intermediate depths, near the oxygen minimum zone and a maximum at about 3000 meters.

Their values are in general lower than those reported here.

They found the waters to be undersaturated at depths as shallow as 190 meters, while Fig. 32 shows undersaturation beginning below 400 meters depth at the latitude of their station. This difference is due to the higher pH values measured during Surveyor 1968 Spring

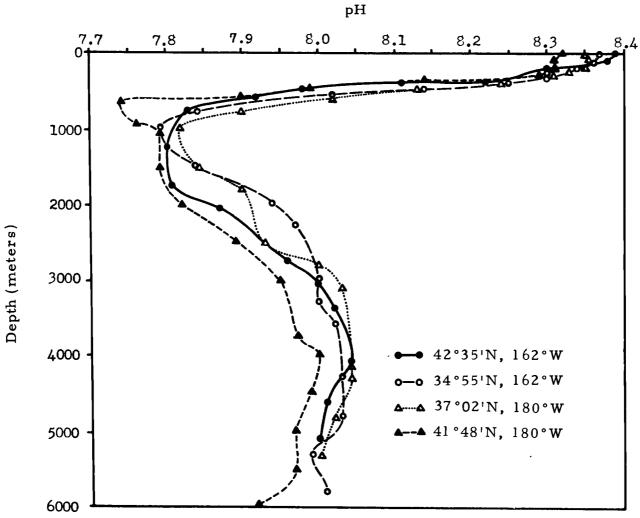


Fig. 33. Vertical distribution of pH at four stations of Surveyor 1968 Spring cruise.

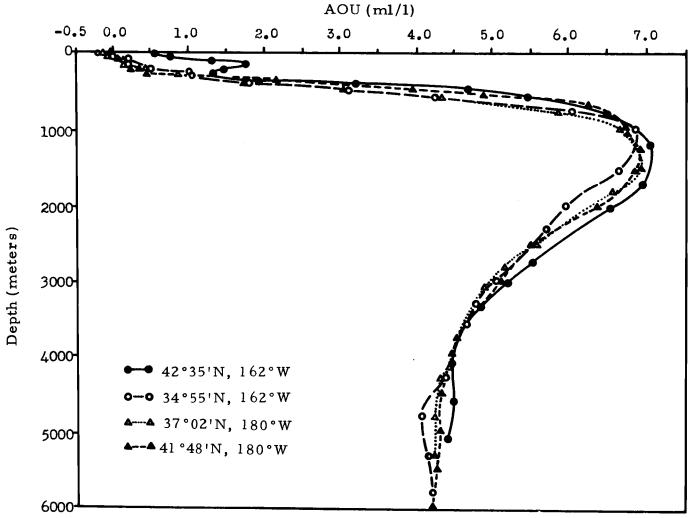
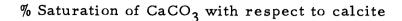


Fig. 34. Vertical distribution of AOU at four stations of Surveyor 1968 Spring cruise.



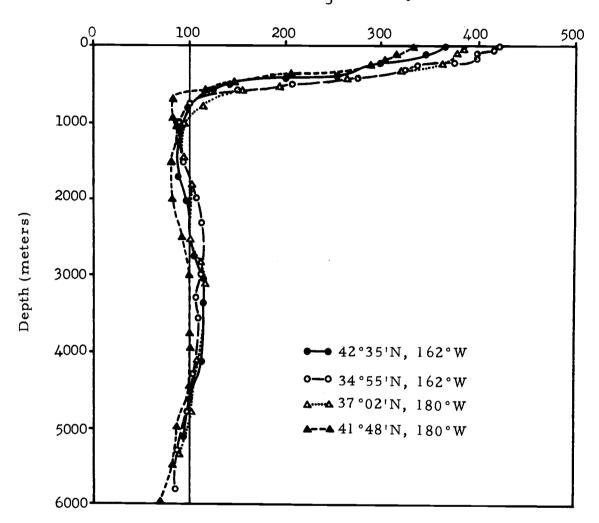


Fig. 35. Vertical distribution of the percent saturation of calcium carbonate with respect to calcite at four stations of Surveyor 1968 Spring cruise.

cruise. Comparing pH values for a depth of about 5000 meters from YALOC 66 cruise and Surveyor 1968 Spring cruise we can see that those from the latter are about 0.2 of a pH unit higher than those from the former. Differences like this are not likely to be real at these depths. Higher pH values give higher percent saturation of calcium carbonate values. Another reason for the disagreement at depths shallower than 1000 meters is that AOU was higher during YALOC 66 cruise than during Surveyor 1968 Spring cruise (Fig. 34) because YALOC 66 cruise was in summer when higher AOU causes lower pH and thus lower values of percent saturation of calcium carbonate.

## SUMMARY

- 1. In both sections, along 162°W and 180°W, the vertical distribution of the physico-chemical parameters is such that in general there is a tendency for the isograms to slope upward from south to north following the same trend of the sigma-t surfaces.

  This indicates that mixing and advection along the sigma-t surfaces play an important role on the distribution of these parameters.
- 2. The vertical AOU distribution at about 50°N, shown by data from one station of Surveyor 1968 Spring cruise compared to that shown by one station of YALOC 66 (summer) cruise, indicates that aeration by mixing, eddy diffusivity and conductivity takes place to more than 500-meter depth.
- 3. The distribution of preformed phosphate on the 27.3 sigma-t surface suggests that there is no detectable mixing at this density surface. But its distribution on the 26.8 sigma-t surface indicates that mixing is occurring in the north-south direction. Due to the low precision of the preformed phosphate data its distribution does not show on the sigma-t 27.3 surface the evidence of mixing that the minimum salinity and temperature show.
- 4. The direction of flow suggested by the AOU distribution on the 26.8 sigma-t surface agrees with that indicated by the geo-strophic method, except in two cases. Farther south than about 42°N

AOU distribution indicates a relatively small southward component of flow that is not indicated by the acceleration potential. This could be caused by a gradient of organic primary production at the sea surface of this southern region with higher production at lower latitudes. At the northern part, between 175°E and 180°W, AOU distribution indicates a linkage between the westward flow south of the Aleutian chain and the eastward flow farther south. This linkage is not indicated by the acceleration potential. If the pattern of flow at the 26.8 sigma-t surface, which at these latitudes is at about 200 meters depth, is similar to that at the sea surface, the flow suggested by the AOU distribution is real and there is a linkage between the westward flow and the eastward flow on this density surface.

5. The direction of flow suggested by the AOU distribution on the 27.3 sigma-t surface agrees with that indicated by the geostrophic method with the exception that the westward flow near the Aleutian chain is not indicated by the AOU distribution. This may be due to the fact that the oxygen minimum zone is at this density surface at 50°N, and the oxygen concentration is so low, 0.5 ml/l, that further oxidation decreases it by a very small amount. There is, therefore, no appreciable gradient of AOU with change of longitude to detect the flow south of the Aleutian chain.

6. At 50°N undersaturation of calcium carbonate with respect to calcite was observed to begin from a depth of about 400 meters, and at 35°N it was observed to begin at 800 meters. From about 2000 meters depth to about 5000 meters depth the waters are saturated or slightly oversaturated. Below 5000 meters depth the waters are undersaturated due to the increasing effect of pressure on the solubility product of calcium carbonate and on the pH.

## SUGGESTIONS FOR FUTURE WORK

- 1. To understand more clearly the processes that are occurring in the central North Pacific Ocean it is necessary for future studies to cover a broader area to have a more complete picture before making any interpretation of the distribution of the data.
- 2. To make clear the relation between the Dichothermal (temperature minimum) and the Subarctic Intermediate (salinity minimum) waters it is necessary to make a detailed study of the vertical structure of salinity, temperature and sigma-t to a depth of about 500 meters at different longitudes throughout the North Pacific Ocean.
- 3. To relate the temperature and salinity minimum found at the 27.3 sigma-t surface to a salinity minimum at the sea surface similar to that found by Favorite and Hanavan (1963), and to explain why a salinity and temperature minimum was not found at the 26.8 sigma-t surface, more detailed studies of the salinity and temperature distribution at different sigma-t surfaces and at the sea surface for different seasons need to be done.
- 4. Temperature, light intensity and chlorophyll data, or any other parameters indicating the organic primary production throughout the euphotic zone, as well as some parameters indicative of the mixing process, are necessary. We need to correlate them in a

quantitative approach to decide which process is more important in causing oversaturation of the waters, with respect to oxygen content.

5. Productivity data is also needed to correlate the horizontal gradients of organic primary production with the distribution of AOU and the direction of flow indicated by the geostrophic topography.

This needs to be done at different sigma-t surfaces for different seasons, mainly winter and summer.

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