This thesis covers a wide area of the North Pacific Ocean, latitudinally from 10° to 55°N and longitudinally from Japan to the U.S. coast. With two longitudinal cruises as the main data sources and selected literature data sets as supplementary data source, the distribution of physical and chemical properties in the North Pacific Ocean is presented.

AOU, pH, total CO$_2$, and nutrients (nitrate and phosphate) are interrelated parameters. Along our two longitudinal sections they all show a core structure underlying the salinity minimum layer. From these oxidation related parameters we obtain a conclusion that the subsurface water of the eastern North Pacific Ocean is older than that of the western North Pacific Ocean. Alkalinity, calcium, and silicate show a monotonically increasing trend with depth to the deepest sampling depth.

The alkalinity data can be used as a water mass tracer.
Different water masses which show their own mixing trends can be identified when the correlation of normalized alkalinity with temperature is scrutinized. The vertical distribution of the normalized alkalinity shows a maximum core at a depth of about 2500 m in the North Pacific Ocean. Not only the calcium carbonate dissolution but also the circulation in the deep and bottom layer plays a role in this normalized alkalinity maximum core.

Our analysis of carbonate data shows that about 25% of the increase in total inorganic CO$_2$ of deep water, after leaving from the Southern Ocean to the North Pacific, is contributed by inorganic CaCO$_3$ dissolution. There is no significant difference of inorganic carbon/organic carbon ratio between our two sections. However, it was found that the eastern section has a higher total TCO$_2$ input than that of the western section.

The degree of saturation with respect to calcite and aragonite was calculated from all the available data sets. Mr. Ahmed Rushdi and Professor R.M. Pytkowicz are working on the effect of Mg on the formation and the properties of magnesian calcites. There are metastable forms of these compounds which may have been interpreted as stable ones in solubility determinations. Some revision of degree of saturation may be called for in the future.

Four selected cross-sections, three longitudinal and
one latitudinal, show that a large volume of the North Pacific is undersaturated with respect to CaCO$_3$. The saturation horizon generally shows a shoaling from the west to the east and from the south to the north in the North Pacific Ocean. It was found that lysocline falls on a depth much deeper (about 2500 m deeper) than the saturation horizon of calcite and several hundred meters shallower than the CCD (calcium carbonate compensation depth) depth. Our results support the kinetic point of view on the CaCO$_3$ dissolution mechanisms.

The direct approach on the fossil fuel increase signal in seawater is adopted in this thesis. A new set of preformed equations of alkalinity and total CO$_2$ was obtained from a more updated GEOSECS data. Our results show that the penetration depth of fossil fuel CO$_2$ is strongly related to the surface oceanographic circulation. The shallowest penetration depth is less than 300 m found in the eastern equatorial region where the upwelling prevails and the deepest penetration depth is deeper than 2000 m off Japan where an interaction of Oyashio and Kuroshio currents is found.
Carbonate Chemistry of the North Pacific Ocean

by

Ching-Ling Wei

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I have been very fortunate through these years at OSU in having so many kind and helpful friends. I would like to show these people my sincere appreciation by acknowledging them here. Prof. R. M. Pytkowicz has always been a respected advisor. He not only gives valuable suggestions but also offers tremendous understanding. Without his spiritual support and encouragement I would not have been able to complete this thesis.

I also acknowledge Dr. Arthur Chen's advise in my research work for the first two years as a Masters student and his pH and TA measurements and collection of Ca samples on the Miller Freeman 1981 cruise. E. Olson's pH and TA measurements on the Discoverer 1982 cruise is warmly appreciated. Permission from Dr. R. Feely and Dr. J. Cline for Dr. Chen and E. Olson to participate in the Miller Freeman and Discoverer cruises and their providing hydrographic data plus the calcium data from the Discoverer cruise are acknowledged.

I warmly appreciate my discussions with Celeste Correia and her corrections of my English throughout this thesis. Celeste's encouragement and friendship are extremely important to me. Sincere thanks is extended to Dr. Michael
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Carbonate Chemistry of the North Pacific Ocean

1. Introduction:

The carbonate system in natural waters is one of the most complex topics in oceanography. The system has long interested many oceanographers from various fields since all three subspheres of the earth (biosphere, lithosphere, and hydrosphere) play an important role in the carbonate system.

More recently, the fate of fossil fuel CO₂ in the ocean has promoted interest in the study of carbonate chemistry in the oceans. With the refined determinations for the various dissociation constants of carbonic and boric acids in seawater and the sophisticated instrumentation for measuring the parameters, our knowledge of the CO₂-carbonate system of the ocean has rapidly increased.

The extensive oceanographic investigation has been carried out in the North Pacific Ocean. Those extensive studies, especially in physical oceanography, have provided an excellent knowledge as a foundation for any other type of study such as that of the CO₂-carbonate system.

The purpose of this thesis is to present the results of carbonate chemistry, carbonate-related chemistry, and the relationship of carbonates and CO₂ with geochemical and physical mechanisms in the North Pacific Ocean. In chapter 2, the sources of data used in this thesis is introduced. In chapter 3, the hydrographic background is provided before
the main body of the thesis. In Chapter 4, the carbonate chemistry and related topics are scrutinized as separate units.

Many figures used in this thesis were generated for a forthcoming Department of Energy report (Chen, Wei, Rodman and Olson, in preparation).
2. Data sources:

2.A. Outline of main data source:

The principal data set used in this study consists of two separate NOAA's Miller Freeman (Feely, 1981) and Discoverer (Cline, 1982) cruises. They were in the North Pacific, roughly at longitude along 150°W from June to July 1981 and along 165°E from May to June 1982. Along with carbonate chemistry data, the standard oceanographic values of temperature, salinity, oxygen, and nutrients were measured (Feely, 1981; Cline, 1982).

Data from the Miller Freeman consisted of hydrographic casts of 10 to 15 sampling intervals down to roughly 2500 m. The Discoverer carried out the sampling to a deeper depth down to roughly 3000 m. Measurement of pH is available for 9 stations of the Miller Freeman and for all the stations of the Discoverer. Alkalinity data is available for all the Miller Freeman and Discoverer expeditions. Calcium data is available for all the stations of the Miller Freeman and 8 stations of the Discoverer (Feely, 1982).

The tracks for both cruises are shown in Fig. 1. The cruise tracks for supplemental data can also be found in the figure. The cross-sections, indicated by solid lines, will be discussed in the text.
Fig. 1 Locations of the stations where chemistry data are available. The solid lines connecting the stations indicate the cross-sections discussed in the text. The abbreviations used for the expeditions are - ENP (Miller Freeman), WNP (Discoverer), GS (GEOSECS), IP (INDOPAC).
2.B. Methods of data analysis:

The analytical procedures in measuring the pH and alkalinity used in Miller Freeman expedition were described fully in Chen (1982). Same procedures were used for 1982 Discoverer by Olson and for 1984 INDIVAT I by Chen and Wei.

The pH was measured at 25±0.02°C. Calibration was carried with NBS 4.004 and 7.415 buffers. Alkalinity analysis were performed using the potentiometric titration method of Dyssen and Sillen (1967), modified by Edmund (1970). Calcium samples were taken by Chen on the Miller Freeman cruise and were measured by Mrs. Quan Wu at Oregon State University by using the complexometric titration method (Tsunogai et al., 1968b; Olson and Chen, 1981). Calcium data of Discoverer cruise was obtained by Feely (1982).

2.C. Literature data source:

Two other data sources supplemented the two cruises, Miller Freeman and Discoverer data. The major one was the Pacific GEOSECS (Geochemical Ocean Sections Study) data from 1973-1974. Undoubtedly, the extensive GEOSECS expedition was a milestone in the study of the CO₂-carbonate system. It provided a large data base with high precision. Broecker and
Takahashi (1978) suggested that a correction of -15 μeq/kg of GEOSECS titratiometric total CO₂ data of the Pacific Ocean is needed to achieve the internal consistency of the total alkalinity, total CO₂ and PCO₂ data. The revised carbonate data (Takahashi et al., 1980) will be used for the following discussion. The precision for the GEOSECS alkalinity and total CO₂ data was estimated to be ±0.2% and 0.5% (1σ), respectively, for the Pacific Ocean data based upon the deep water (>4000 m) sample measurement (Takahashi et al., 1981). An updated equation of state (Millero and Poisson, 1981) was used to recalculate density of seawater from all the GEOSECS depth, salinity, and temperature data. The station network is rather coarse but the number of levels sampled and of parameters measured is extensive.

The INDOPAC data (1978) along 35°N provided a high quality close station spacing to couple with our two N-S sections. Some Japanese data (Hattori, 1977) from the Northwest Pacific Ocean (KH75-4) was also used.

In order for a data set to be used for supplemental coverage, it had to have the full array of water chemistry or at least as extensive an array as our cruises. The data generally had to be recent in order to match the quality of the presently obtained chemistry data. In some areas where there was poor station coverage such as the Gulf of Alaska
these criteria were relaxed.

The carbonate data of the Miller Freeman and Discoverer cruises were compared with the literature data sets. It was found that both Miller Freeman and Discoverer data sets and GEOSECS Pacific data are consistent with each other in oxygen, alkalinity, and total CO$_2$. The calculated total CO$_2$ of the Miller Freeman and Discoverer cruises is also consistent with the GEOSECS measured total CO$_2$ data. However, INDOPAC alkalinity data seems systematically lower than the other data sets by 10-15 μeq/kg. The INDOPAC alkalinity data are adjusted to agree with our data sets when used.

2.D. Abbreviations used for data sets:

For the purpose of convenience the abbreviations listed below are used in this thesis for the following discussion:

- GS - GEOSECS expedition
- IP - INDOPAC expedition
- ENP - Eastern cross-section along 150°W from Miller Freeman 1981
- WNP - Western cross-section along 165°E from Discoverer 1982
3. Hydrography:

3.A. Background:

Our study covers an area north of 10°N to 55°N, in which two large-scale gyres appear in the surface wind-driven layer. There exist good reviews of these gyres in literature (Sverdrup et al., 1942; Tully, 1964; Masuzawa, 1972). These two gyres, subtropical and subarctic, play an important role in our study area.

A simple description is presented. The clockwise subtropical gyre, of which the north edge lies in the west wind drift centered at about 40°N, is bounded to the north by North Pacific Current, to the east by California Current, to the south by North Equatorial Current, and to the west by Kuroshio Current. The subtropical gyre exhibits westward intensification and a sluggish eastern equatorward flow. The anti-clockwise subarctic gyre has a smaller size than the subtropical one. The western boundary current, Oyashio, serves as a west boundary for the gyre. An eastward Subarctic Current forms the southern portion of the gyre. Much of the water of the Subarctic Current flows north to be recognized as the Alaska Current off the coast of Canada. The Alaska Current flows westward along the Aleutian Islands. This current is called Alaska Stream (Dodimead,
Below the layer of the surface circulation system a salinity minimum water called North Pacific Intermediate Water (NPIW) is found. The origin and distribution of the NPIW has been extensively discussed by Reid (1965). It appears to circulate in a clockwise gyre and its relatively high oxygen content indicates frequent replenishment.

The deep water of the North Pacific, underlying the NPIW, is characterized by very uniform properties. The source, path, and modification of the deep and bottom water of the North Pacific can be reviewed from the existing literatures (Knauss, 1962; Reid and Lynn, 1971; Edmond, Chung and Sclater, 1971; Mantyla, 1975; Mantyla and Reid, 1983). In summary, the bottom water flows from the Southwest Pacific Basin to the Central Pacific Basin through the Samoan Passage near 100S, 1690W. Part of this south origin water spreads from the Central Pacific Basin to the north through the Wake Island Passage into the Northwest Pacific Basin and to the east into the Northeast Pacific Basin.

A schematic diagram shown in Fig. 2 serves as a summary for the oceanographic circulation and water masses found in the North Pacific Ocean. In the surface wind-driven layer, a water mass called North Pacific Surface Water (NPSW) can be
Fig. 2 Schematic diagram of water masses distribution of the North Pacific Ocean.
divided, by a frontal zone, into North Pacific Subarctic Water (NPSA) and North Pacific Subtropical Water (NPST) according to the characteristic physical properties. Underlying the NPSW, a water mass called NPIW characterized by a salinity minimum is found. Two deep water masses, North Pacific Deep Water (NPDW) and North Pacific Bottom Water (NPBW), are found below the NPIW.

3.B. Inferences from this work:

Vertical cross-sections of the measured variables were prepared for both longitudinal sections occupied by the Miller Freeman (Feely, 1981) and Discoverer (Cline, 1982) data.

Salinity

Fig. 3 and 4 show the vertical distribution of salinity (S) for the ENP (Feely, 1981) and WNP (Cline, 1982) data, respectively. The depth distribution of the S for both ENP and WNP sections shows a deepening in the Central Pacific and shallowing approaching the equator. This results from the general surface convergence of water towards the center of the anticyclonic gyre and thus deepens the isopleths in mid-latitudes. In the equatorial regions upwelling results which carries properties closer to the sea surface.

The vertical section of salinity for the ENP section
Fig. 3  Distribution of salinity with depth along the 150°W cross-section (Data from Feely, 1981).
Fig. 4 Distribution of salinity with depth along the 165°E cross-section (Data from Cline, 1982).
Fig. 3) shows the development of a shallow salinity maximum extending southward from the vicinity of the subtropical front where evaporation is high (Tsuchiya, 1968). Its depth is at approximately 100 m and salinities exceed $34.8 \times 10^{-3}$. WNP data also shows a shallow salinity maximum extending southward from about $25^\circ N$ to about $18^\circ N$ (Fig. 4). This S-maximum is not as clear as the ENP section presented above but shows more saline characteristics (saltier than $35.2 \times 10^{-3}$).

The salinity section of ENP along $150^\circ W$ shows a broad frontal feature from $35.00 \times 10^{-3}$ to $33.25 \times 10^{-3}$ and extending from $31^\circ N$ to $39^\circ N$ (Fig. 3). Thus, on the basis of surface salinity, the subarctic front appears to be located near $39^\circ N$ and the subtropical front near $31^\circ N$.

Salinity structure along the WNP section (Fig. 4) is more complicated than that of the ENP section. A highly advective region is shown by a zig-zag salinity contours from $35^\circ N$ to $40^\circ N$ down to a depth of 1500 m. The deepening of salinity contours at this region and the upwelling in the equatorial and in the northern North Pacific make the salinity structure show an overall concave pattern along the cross-section. Two sharp horizontal salinity gradients in the surface layer are found respectively at $43^\circ N$ and $37^\circ N$. They were identified as the subarctic front at the north and
as the subtropical fronts at the south, respectively (Dodimead et al., 1963; Masuzawa, 1972).

Two shallower salinity minimums have been investigated in the Northeast Pacific by Reid (1973) which have an analogous origin. Using STD data, Kenyon (1978) has found the shallow salinity minimum in the upper 200 m to be extensive and continuous in the eastern Pacific from 125°W and 175°W along 35°N. It is likely that the fresher near-surface waters north of 40°N contain these layers but the sampling interval for our data was not sufficiently detailed to delineate them.

On both longitudinal sections the predominant north/south feature is the low salinity deep stratum which is situated near the surface in the north. It deepens and appears as a salinity minimum tongue at about 600 m at mid-latitudes, then shallows towards the equator.

The origin and distribution of the deep salinity minimum has been extensively discussed by Reid (1965) who found that it originated in the northwest Pacific north of 45°N in the Sea of Okhotsk and in the vicinity of Kamchatka Peninsula. Reid (1965) has shown the salinity minimum water mass originates from winter time convection and subsequent vertical diffusion to the density levels associated with this deep S-min. These density levels are nearest the
surface in the northwest Pacific. Winter convective overturning and vertical diffusion subsequently maintain the salinity minimum. However, the minimum may result from the formation of warmer and more saline waters above it in summer.

In the ENP section of 150°W, the major salinity-minimum core (values from about 33.75 to 34.20 x 10^{-3} N to S) begins to appear near 45°N and is associated with the 26.8 δθ surface at a depth of about 300 m. It deepens southward to about 500 m and then rises to near 400 m at 15°N (Fig. 3). In the WNP section of 165°E, the clear salinity minimum core associated with δθ = 26.8 centered at depth of 400 m at 40°N and deepens into a depth of 700 m at 37°N is shown in Fig. 4. This S-minimum core becomes shallower into a depth of 300 m at 20°N. The salinity at this tongue-like core increases from 33.8x10^{-3} to 34.2x10^{-3} to the south.

Temperature

Fig. 5 shows the vertical distribution of potential temperature (θ) for the ENP data (Feely, 1981). Fig. 6 shows the vertical distribution of temperature (T) for the WNP data (Cline, 1982).

The overall trend to the isotherm on Fig. 5 is a general upward slope to the north so that for any level shallower
Fig. 5 Distribution of potential temperature with depth along the 150°W cross-section (Data from Feely, 1981).
Fig. 6 Distribution of temperature with depth along the 165°E cross-section (Data from Cline, 1982).
than roughly 2000 m the temperature is usually less to the north, which is consistent with the accepted view of heat input in the equatorial regions of the oceans (Pickard, 1979).

There are exceptions to this general inclination. South of about 20°N the isotherms warmer than about 10°C shallow towards the equator which is typical for isopleths which upwell in equatorial waters (Tsuchiya, 1968; Craig et al., 1981).

In Fig. 5, two regions of maximum surface temperature gradients are noticeable. A southerly gradient near 35°N centered on about the 17°C isotherm corresponds to the subtropical front; and a northerly gradient near 43°N centered on the 11°C corresponding to the subarctic front. Hence the temperature transitional zone is shifted several degrees northward compared to the salinity front.

Fig. 6 shows a more complicated isotherm structure for the WNP section than that of the ENP section. The isotherm between 35°N and 40°N shows a zig-zag like structure to a depth of about 1500 m. This results from the active interaction of two major western boundary currents (Oyashio and Kuroshio) which have large differences in temperature. North of 40°N the isotherms have a general upward slope to the north. South of 20°N two different general inclinations
are observed. The isotherms warmer than $8^\circ$C shallow toward the equator, which is the result of equatorial upwelling.

**Density**

The potential density ($\sigma_\theta$) is calculated from depth, $S$, and $T$ for ENP (Feely, 1981) and WNP (Cline, 1982) data and is plotted with depth (Figs. 7 and 8).

In the mid-latitude the isopycnals show a deepening relative to stations in the north or the south. This deepening shifts northward with depth so that the deepening of the $26.00 \sigma_\theta$ isopycnal occurs near $26^\circ$N and the $27.50 \sigma_\theta$ isopycnal occurs near $41^\circ$N for the ENP section. The potential density structure for the WNP section is similar to that of the ENP section. However, the shifting of deepening sites of the isopycnal is not as clear as the ENP (Fig. 7) for the WNP (Fig. 8) section.

Fig. 8 shows $26.0 \sigma_\theta$ contour has a steep slope at about $37^\circ$N. This water corresponds to the Kuroshio Extension and was proposed by Masuzawa (1972) to be the Subtropical Boundary. It is important to note that WNP20 was located at $175^\circ$E (Fig. 1) where the $26.8 \sigma_\theta$ isopycnal does not outcrop. Note the change in contour intervals for densities greater than $27.00 \sigma_\theta$. The densest water existing on these cross-sections is $27.74$. 
Fig. 7 Distribution of potential density ($\sigma_\theta$) with depth along the 150°W cross-section (Data from Feely, 1981).
Fig. 8 Distribution of $\delta_\theta$ with depth along the 165°E cross-section
(Data from Cline, 1982).
**Θ-S diagram**

Figs. 9 and 10 show a full scale and expanded scale ENP Θ/S distribution. Fig.11 shows the Θ/S distribution for selected GEOSECS stations in the North Pacific. The Θ-S correlation for the WNP data is shown in Fig.12 and the expanded Θ-S correlation for the same stations is shown in Fig.13. The Θ-S relationships for all the stations differ from each other in the upper layer, but converge to the same Θ-S relationship at greater depths.

The stations nearest to each other on the two cruises are GS204 (31°22'N, 150°2'W) and ENPI3 (32°1'N, 150°2.1'W). The Θ/S correlation of GS204 was also plotted in Fig.9. Both ENPI3 and GS204 show similar Θ/S structure but ENPI3 is somewhat saltier above the salinity minimum and has an approximately 1°C warmer salinity minimum.

It is noticeable in both Figs. 9 and 12 that the Θ/S of surface mixed layer shows a general conservative mixed between two water types, NPSA and NPST. The water between the mixing layer and salinity minimum layer for the southerly stations of both ENP and WNP data also show a linear mixing structure.

WNP20, analogous to Edmond's (1974) SEVENTOW7-178 station, shows the linear Θ-S region extends from the surface to the deepest sampling depth. The intensive
Fig. 9 θ-S correlation for ENP and selected GS data (Data from Feely, 1981) and related GS data.
Fig. 10 Expand $\theta$-$S$ correlation for ENP data (Data from Feely, 1981).
Fig. 11 θ-S correlation for selected GS data.
Fig. 12  $\theta$-$S$ correlation for WNP data (Data from Cline, 1982).
Fig. 13 Expanded $\theta$-S correlation for WNP (Data from Cline, 1982) and selected KH75-4 data.
upwelling may be the main mechanism for this observation.

A potential temperature minimum at $S = 33.2 \times 10^{-3}$ is observed at WNP18. In order to show the source of this temperature minimum core, $\theta$-S of three Japanese KH75-4 Hakuho Maru stations are used (Fig. 13). KH75-4-7 and KH75-4-6 located near the Kamchatka Strait, one in and one out of the Bering Sea (Fig. 1). WNP18 and two Japanese stations all show a thermocline, which is believed to be caused by summer heating of the surface layer. The temperature minimum core is also found for these two stations. This core falls on the isopycnal surface of $\delta_\theta = 26.5$. This temperature minimum water is proposed to be the remnant Bering Sea winter water. The core of temperature minimum is similar to the dichothermal temperature in the Bering Sea (Tully, 1964). The dichothermal structure results from existence of the residue of the winter cooled water lying in between the upper seasonal and deep permanent halocline. The winter remnant water may flow out from the Bering Sea along the isopycnal $\delta_\theta$ surface of 26.5. The linkage between this temperature minimum water and salinity minimum water found in more southerly stations needs to be studied further.

In the GEOSECS network samples the northwestern Pacific, a temperature-minimum structure is seen at GS218.
which is not present on the 150°W ENP section. The most northerly stations (Fig.9) show a general continuous increase of salinity with decreasing temperature (and hence depth) below the mixed layer. Proceeding southward the salinity-minimum layer develops and becomes most pronounced in the central North Pacific region of the section at ENP13, 14, 16, 19. The most southerly, ENP22, shows practically no reduced salinity signature in the strata containing the salinity minimum on the stations further north. This is especially noticeable in Fig.10 which shows expanded θ-S correlation for ENP data. A deep salinity minimum is also noticeable in Fig.12. Three most northerly stations, WNP16,18,20 show no salinity minimum core property. Like ENP data, the salinity minimum core is diminished for the northerly stations, WNP16,18,20.

The deepwater at temperatures below 1.5°C is quite uniform (Figs.10 and 13) and this is particularly evident for the GEOSECS data (Fig.11) where sampling depth extends to the bottom. However between the salinity minimum strata at roughly 5°C to 6°C and the temperature 1.5°C (depth~1500 m) there are two separate distinct curves to the θ/S distribution. This is seen in both the Miller Freeman and Discoverer data (Figs.9 and 12) particularly on the expanded scale relationship (Figs.10 and 13) and in the GEOSECS data.
(Fig. 11). The northerly stations with no salinity minimum, or showing the beginning of the salinity minimum (ENP2, 4, 6, 8, 10; WNP16, 18, 20, and GS221, 219, 218), are significantly fresher on any given isotherm.
4. Results and discussions:

4.A. Chemistry data along 150°W and 165°E

The results of carbonate data and related chemistry data for the ENP and WNP expedition are shown by longitudinal sections. Following the discussion of the various chemistry data along the two cross-sections, the correlation of Θ and S with various carbonate parameters will be used to scrutinize the distribution of the parameters.

4.A.(a) AOU and pH:

The oxygen distribution for ENP is similar to that made by the others (Smetanin, 1962; Postma, 1964; Reid, 1965; Duedall and Coote, 1972). The presence of oxygen minimum is a reflection of the North Pacific circulation system where oxygen decreases downstream from its aeration source and replenishment is primarily by vertical diffusion (Reid, 1965).

Apparent Oxygen Utilization (AOU) is a rough measure of the amount of oxygen consumed by oxidation since the waters left their surface source. It is calculated by the difference between the solubility of oxygen at the potential temperature and salinity, and the measured oxygen concentration. We assume that a parcel of seawater was at equilibrium with the atmosphere before it sank. Hence, a
negative AOU of seawater means oversaturation with respect to the atmospheric oxygen while the positive AOU means undersaturation.

As shown in Fig. 14 which shows the vertical distribution of AOU along the ENP section, most surface water is oversaturated with respect to atmospheric oxygen. The 100% saturation horizon outcrops between ENP2 and ENP4. Like that described by Postma (1964), the ocean shifts from an oxygen source into an oxygen sink at about 55°N. AOU's were found to be useful to study the direction of water motion in the North Pacific Ocean (Pytkowicz and Kester, 1966; Park, 1967; Alvarez-Borrego and Park, 1971). Fig. 15 shows the distribution of AOU with δθ along the ENP section. This figure shows a diapycnal character at densities less than 27.3. The maximum AOU enters along 27.4 δθ from the north as a greater than 300 μM/kg tongue. The corresponding depth is about 1200 m (Fig. 14). Continuing south to 15°N the maximum is greater than 280 μM/kg and along the same strata. Reid and Mantyla (1978) show that the low oxygen water in this depth range (δ_{1000} = 32.0, i.e. density reference adiabatically to 1000 db which is approximately δθ = 27.35) enters as a tongue from the east roughly between 45°N and 30°N. Thus the motion, or rather the direction of older waters, for the water at this level is towards the west for
Fig. 14 Distribution of apparent oxygen utilization (AOU) with depth along the 150°W cross-section (Data from Feely, 1981).
Fig. 15 Distribution of AOU with δθ along the 150°W cross-section (Data from Feely, 1981).
most of this cross-section.

Figs. 16 and 17 show the distribution of AOU with depth and $\delta_{18}^O$, respectively, along the 165°E cross-section. The AOU distribution of WNP is similar to that of the ENP section except several points. The AOU value for the water below a depth of 1000 m of WNP (Fig. 16) seems to be lower than that of ENP (Fig. 14). According to Pytkowicz and Kester (1966), the gradients of AOU indicates the relative ages of the waters. Thus, the water below 1000 m for ENP is proposed to be older than that of WNP. The carbon-14 data in the North Pacific also support the older age of the deep water of the eastern North Pacific Ocean than the western North Pacific Ocean (Fiadeiro, 1982). There is another difference between the AOU distribution of ENP and of WNP. A sharp AOU vertical gradient for the water above 300 m is found in the north of WNP section. There is no identical phenomenon found in the ENP section. An active upwelling process must exist at WNP20. This is similar to the findings of Dodimead et al. (1963) and Park (1967).

Distribution of pH(25°C) with depth for ENP data along 150°W is shown in Fig. 18. pH distribution has a similar pattern with AOU (Fig. 14). A tongue-like minimum core of pH extends equatorward. The 7.5 contour reaches to 25°N. The axis of pH minimum deepens at 40-50°N to a depth of about
Fig. 16 Distribution of AOU with depth along the 165°E cross-section (Data from Cline, 1982).
Fig. 17 Distribution of AOU with $\delta^0$ along the 165°E cross-section (Data from Cline, 1982).
Fig. 18 Distribution of pH(25°C) with depth along the 150°W cross-section.
1200 m and becomes shallower equatorwardly to a depth of 800 m at 25°N and poleward to a depth of 700 m. The surface pH value decreases northward, which is the result of a high partial pressure of CO$_2$ because of higher solubility of CO$_2$ in the colder north region.

The pH(25°C) data of the WNP section are plotted in Fig. 19. This section is very similar to the ENP section. The surface pH value increases from north to south. The isopleth in surface layer shows a concave pattern. A clear pH minimum core centered at 1000 m extends equatorward.

Fig. 20 shows correlation of Θ and pH(25°C) for the ENP cruise. All the pH data from ENP and WNP cruises has a minimum. From this figure, we can see the difference of pH minimum between ENP16,19 and the others. The pH minimum of former stations is about 7.5, while the pH minimum of the other stations is about 0.05 pH units lower than two southernmost stations. The minimum pH value of two southernmost stations are lying on about 4°C while the pH minimums of the other stations are lying on about 3.5°C. This difference depicts a different history of the pH minimum waters of these two groups of stations. The pH minimum water of northerly group stations is older, colder, and more corrosive than that of ENP16,19. Fig. 21 shows the same correlation for the WNP stations. The two sections, ENP
Fig. 19 Distribution of pH(25°C) with depth along the 165°E cross-section.
Fig. 20 Correlation of $\Theta$ with pH(25°C) for the ENP stations.
Fig. 21 Correlation of \( \theta \) with pH(25°C) for the WNP stations.
and WNP, have similar θ-pH correlations. Two southernmost stations, WNP3,5, show the same characteristics as ENP16,19. However, WNP3,5 have higher pH minimum values of about 7.6 than that of ENP16,19. Hence, the water at the pH minimum layer of ENP is older than that of WNP. The northernmost station, WNP20, shows a relatively homogeneous temperature layer with a large range of pH value (from 7.35 to 7.67). Park (1968a,b) also found this phenomenon at near-by site. He attributed this large variation of pH value to be mostly due to the organic decomposition and that an upwelling mechanism brings this cool and acidic water to the surface layer.

Figs. 22 and 23 show the S-pH(25°C) correlation for ENP and WNP data respectively. The S-pH correlation shows better mixing characteristics for surface water than that which was shown in θ-pH correlation. The important factors that control the pH value for surface water are temperature, salinity, biological activity, TA, and saturation relative to the partial pressure of CO₂ in the atmosphere. For the WNP cruise, surface pH(25°C) increases from 7.95 at the northern latitude to 8.30 at the southern latitude. For the ENP cruise, surface pH(25°C) increases from 8.00 at the north to 8.25 at the south. The surface pH values for those stations located in between the two southernmost and
Fig. 22 Correlation of $S$ with $\text{pH}(25^\circ C)$ for the ENP stations.
Fig. 23 Correlation of S with pH(25°C) for the WNP stations.
northernmost stations fall on the linear trend connected by two end members. This linear trend cannot be explained theoretically. Such an increasing pH trend from high to low latitude was also observed by Park (1966) in the region of the Northeastern Pacific Ocean. Wider pH range simply due to wider T range.

Since pH is not a conservative property, it cannot be used as a parameter to study the mixing phenomenon. However, the coil-like pattern of S-pH plots (Figs. 22 and 23) shows a characteristic water-type property. The NPSW with a linear S-pH correlation, NPIW with salinity minimum layer for northerly stations, NPDW with pH minimum value, and NPBW as the end of increased pH trend, make up of this coil-like pattern.

Park (1968a, 1968b) discussed two factors, AOU and CaCO₃ dissolution, which affect the vertical distribution of pH value. The pH(25°C) and AOU correlation is plotted for both ENP and WNP data (Figs. 24 and 25). ENP pH data apparently shows better precision than that of WNP. The pH minimum generally coincides with the AOU maximum. However, WNP2O shows a significant difference between AOU maximum and pH minimum (Fig. 25). Again, this phenomenon is subject to the complicated involvement of upwelling which may have the atmospheric oxygen entering the upwelled oxygen-depleted
Fig. 24 Correlation of AOU with pH(25°C) for the ENP stations.
Fig. 25 Correlation of AOU with pH(25°C) for the WNP stations.
water. We found a slope of 2.5 pH(pH unit)/AOU(mmol/kg) for the waters below the maximum AOU layer. This slope is higher than the slope obtained by Park (1968b) but still falls in the range of uncertainty. Our shallow sampling depth (3000 m) may cause uncertainty of the overall trend for the deep water. The slope for the water above AOU maximum layer varies from 1.7 to 2.1 depending on the location of the station. Because of the relatively fast exchange rate of oxygen between seawater and the atmosphere, the slope of surface layer is not reliable. Our data covered a wider area which includes oceanographic subarctic and subtropical region than that of Park (1968b). This wide coverage also makes our pH-AOU correlation not as unique as that obtained by Park. However, the average slope of 2.1 ΔpH/ΔAOU is close to the calculated slope of 2.0 ΔpH/ΔAOU obtained by Park (1968b). The lag between two trends, deep water and shallow water, is mainly caused by calcium carbonate dissolution. The schematic arrows are shown indicating the effect of CaCO_3 dissolution and organism decomposition.

4.A.(b) Alkalinity data:

The vertical distribution of normalized alkalinity (NTA=alkalinityx35/S) along 150°W section is shown in Fig.26. The NTA generally increases with depth. A shallow
Fig. 26 Distribution of NTA with depth along the 150°W cross-section.
minimum layer is observed at the region of 37°-50°N. A low NTA pool is found in between the two fronts.

Fig. 27 shows distribution of NTA for WNP data along 165°E. NTA increases monotonically with depth. This is consistent with the work of Park (1967). The surface NTA decrease southward from the subarctic region to the subtropic region. A low NTA pool is found lying between 20°N and 30°N. The NTA contour lines are pushed downward at 20°N. This may be a clue of NPDW intrusion. The alkalinity distribution in the Pacific was found to have a maximum at a depth of about 2500 m (Takahashi et al., 1981; Fiadeiro, 1980). The sampling depth for the WNP expedition, except WNP12, is too shallow to see the maximum. However, a maximum core at a depth of 2500-3000 m is observed at WNP12.

The correlation of potential temperature and normalized alkalinity data is plotted (Figs. 28 and 29) for both ENP and WNP sections and selected stations of the GEOSECS expedition. The purpose of adding GEOSECS stations near our two sections is to show the better correlation by increasing the sample size and to find the NTA distribution for bottom water. Early in 1956, alkalinity was used as a parameter for water mass analysis (Koczy, 1956). From Figs. 28 and 29, we can identify the different trends representing five water masses; NPSW, North Pacific Central Water (NPCW), NPIW,
Fig. 27 Distribution of NTA with depth along the 165°E cross-section.
Fig. 28  Correlation of $\theta$ with NTA for ENP and selected GS stations. The triangles represent surface data and the squares represent salinity minimum data.
Fig. 29 Correlation of $\theta$ with NTA for WNP and selected GS stations. The triangles represent surface data and the squares represent salinity minimum data.
NPDW, and NPBW along the water column. The linear lines in Figs. 28 and 29 are roughly drawn by eyes.

a. NPSW—The NTA distribution of surface water is complicated by physical conditions, biological activity (to less extent), river runoff, and oceanographical circulation. The surface NTA is denoted by triangles in Figs. 28 and 29. Although the data are scattered, a rough linear line is plotted in Figs. 28 and 29. This line represents an increase of 4 μeq/kg for a decrease of 1°C surface temperature. NTA of the subarctic and of the subtropical serve as two ends of the linear line. Low temperature, high NTA water is mainly from the Gulf of Alaska. Both in Figs. 28 and 29, there is a high NTA water for temperatures higher than 25°C. The cause of this anomaly may be related to the equatorial upwelling which contains high alkalinity upwelled from subsurface layer (Fiadeiro, 1980). The 25°C break is consistent with the work of Chen and Pytkowicz (1979), which was based on GEOSECS data.

b. NPCW—Below the NPSW, a layer of water defined as NPCW is identified. The θ-NTA correlation of this layer is also scattered, especially for the ENP data, and shows generally a smaller NTA value than NPSW and NPIW. More scattering of ENP data than WNP data of this water may result from the general circulation pattern which has a
westward intensification and a broad, sluggish eastern flow (Mazuzawa, 1972). The NPCW of the Eastern North Pacific receives more influence of other water masses which have different NTA values to NPCW. In other words, NPCW for WNP retains more original properties and receives less influence from the other water masses. A tentative linear trend is drawn on these waters. The extent of variations of NTA with temperature seems narrower than that of NPSW. The increased trend of NTA is about 3 µeq/kg/°C.

c. NPIW—There is a well-known salinity minimum in the North Pacific Ocean as discussed earlier. This salinity minimum core represents NPIW and is believed to be formed in the western subarctic ocean (Reid, 1965) and circulates roughly in a clockwise pattern (Sverdrup et al, 1942). The NTA at salinity minimum layer is denoted by squares in Figs. 28 and 29. Fig. 29 shows that there is a linear correlation between θ and NTA. This line is also drawn on Fig. 28 on which correlation seems weak. This trend has a steeper slope than overlying NPCW and NPSW, which means a higher rate of "input" of alkalinity (about 5.5 µeq/kg°C). Generally, the NTA of this water has higher NTA than that of NPCW and lower than that of NPSW. This causes a minimum NTA layer in NPCW down the water column. However, this minimum is diminished for the water in the Subarctic region. The
mechanism causing this shallow alkalinity is unknown.

d. NPDW- The NTA in NPDW is characterized by a sharp NTA increase (12 μeq/kg/°C). The NTA value of WNP is lower than that of ENP. Fiadeiro (1980) also found a higher alkalinity for the Eastern North Pacific. In Shiller and Gieskes' (1980) 35°N cross-section, a higher alkalinity value also was observed in the Eastern region. However, the increase rate vs potential temperature does not show significant difference for the two sets of data. The sharp NTA increase is because this water is undersaturated with respect to calcium carbonate (the saturation value vs calcite and aragonite will be discussed later). The dissolution of calcareous materials must occur. The increase of pressure also favors the dissolution of calcareous mineral. The Θ-NTA trends of NPDW and overlying NPIW cross at about 6°C for ENP data and at about 5°C for WNP data.

e. NPBW- NPBW trend cannot be found if only the data of our two sections is used. Thus, the NTA of several GEOSECS stations near our two sections is used to see the distribution of NTA in the bottom layer. The bottom water has potential temperature of about 1.1°C. The NTA decreases dramatically toward the sea bottom. The circulation pattern in the deep North Pacific causes this maximum. Fiadeiro (1980) suggested the effect of vertical eddy diffusion from
the deep water which contains high alkalinity, not of local sources or flux from the bottom. The relationship among NTA distribution, oceanographic circulation, and calcite degree of saturation will be discussed in a later section.

The correlation of salinity with NTA for ENP and WNP stations is shown in Figs. 30 and 31, respectively. S-NTA correlation is more informative for the surface mixing but is less informative for the subsurface mixing. The S-NTA correlation is interestingly T-shaped with a horizontal line representing surface water and a vertical line representing subsurface water. The same finding was observed by Koczy (1956). The knot connecting the two trends is NPIW which has an average salinity of 34.0x10^{-3} and NTA of about 2370 μeq/kg. "Horizontal" means a small variation in NTA and "vertical" means a sharp increase of NTA. The fresh, high alkalinity water is subarctic water and saline, low alkalinity water is subtropical water. The transition zone is located between the two ends and has NTA value between. Beneath the core of salinity minimum, the salinity and NTA increase monotonically to our deepest sampling layer (about 3000 m). A rough linear relationship can be seen on these subsurface S-NTA data. The deviation of S-NTA trend for those stations south of 25°N (ENP16,19,22,26, WNP3,5,6) is caused by the salinity difference. At this layer, southerly
Fig. 30  Correlation of S with NTA for ENP stations.
Fig. 31 Correlation of S with NTA for WNP stations.
stations have higher salinity than that of the others.

4.A.(c) Total CO$_2$:

The total inorganic CO$_2$ for both of our ENP and WNP sections was calculated from the pH and alkalinity data. For 150°W section only ENP2-19 has Total CO$_2$ because pH data is not available for the other ENP stations. The total CO$_2$ for ENP and WNP was calculated from pH(25°C) and TA by using the first and second dissociation constants of carbonic acid of Mehrbach et al. (1973) and dissociation constant of boric acid of Lyman (1957). Fig.32 shows vertical distribution of normalized total CO$_2$ (NTCO$_2$=TCO$_2$×35/S) along 150°W. The distribution is very similar to the distribution of AOU and pH. Since the pH and NTCO$_2$ are strongly related to the production and consumption of the organism in the ocean, the similar contour pattern of the AOU, NTCO$_2$ and pH contours is not surprising. A high NTCO$_2$ core centered at the depth of about 1200 m extends equatorward. The highest NTCO$_2$ is found at a depth of 1200 m at about 43°N. The surface NTCO$_2$ which is strongly affected by the biological activity and surface temperature shows a decreasing trend from the north to the south.

Same NTCO$_2$ contours are constructed for WNP data along 165°E (Fig.33). This section is very similar to the ENP
Fig. 32 Distribution of NTCO$_2$ with depth along the 150°W cross-section.
Fig. 33 Distribution of NTCO₂ with depth along the 165°E cross-section.
section. It is noted that the maximum NTCO$_2$ core is lying at a depth of several hundred meters deeper than that of the AOU maximum core. This gives an impression that the dissolution of inorganic calcareous material also contribute the increase of TCO$_2$.

4.A.(d) Calcium data:

Another important carbonate parameter, calcium concentration, is plotted in Fig.34. The specific calcium (calcium/chlorinity) is known to be useful for studying the water mass circulation, mixing and diffusion in the Pacific Ocean (Tsunogai et al., 1968a; Sagi, 1969; Tsunogai et al., 1973; Horibe et al., 1974; Shiller and Gieskes, 1980). The normalized calcium (NCa=Cax35/S) we use here has the same meaning as that of specific calcium. The NCa increases monotonically from the surface to the deepest sampling depth. In the northern region, the surface NCa decreases southward. A high NCa value of more than 10280 $\mu$mol/kg is found at the deep layer of the Northeast Pacific Ocean, which is similar to Tsunogai's (1973) result. The water here represents the oldest of the deep waters of the world oceans (Knauss, 1962; Mantyla, 1975; Mantyla and Reid, 1983). The calcium content in this water is higher as a result of CaCO$_3$ dissolution. A dome of high NCa is found in the deep
Fig. 34 Distribution of NCa with depth along the 150°W cross-section.
water north of 40°N.

Salinity and NCA for ENP data is shown in Fig. 35. The surface NCa shows scattered patterns on which the clear correlation can not be found. Tsunogai et al. (1968a) found a linear correlation between chlorinity and specific calcium in the region of the Western North Pacific Ocean where the western boundary currents prevail. The lack of clear linear correlation may be due to the complicated biologic uptake and river runoff at the Eastern North Pacific. However, in the region of the Gulf of Alaska the surface S-NCa correlation shows a linear mixing process. The overall trend of S-NCa relation in surface water is increasing calcium with decreasing salinity. Shiller and Gieskes (1980) also found a high NCa in those surface waters of northern origin. In contrast to the surface layer, subsurface water has an increasing NCa trend with increasing salinity. Like alkalinity data, the S-NCa combination of NPIW which has a uniform NCa value of about 10230 μmol/kg, seems to be a connecting knot between two trends, surface and subsurface, of S-NCa correlation. The deviation of two southernmost stations, ENP22 and ENP26, is due to the high salinity in the region of these stations.

Fig. 36 (Θ-NCa correlation) shows a similar pattern as S-NTA correlation for the same stations but more scattered
Fig. 35 Correlation of $S$ with $\text{NCa}$ for ENP stations.
Fig. 36 Correlation of \( \theta \) with NCa for ENP stations. The triangles represent surface data and squares represent salinity minimum data.
especially for the surface water (denoted by triangles). The NCa value increases with decreasing temperature. A break of slope for θ-NCa relationship is coincident with θ-NCa combination of NPIW (denoted by squares) which also shows a slight increasing NCa trend with decreasing θ. NPDW shows a higher slope which means the dissolution of CaCO₃ mineral prevails.

Feely's (1982) calcium data along 165°E is used here. Figs.37 and 38 show the correlation between S-NCa and θ-NCa, respectively. Both figures have similar patterns as ENP's pattern (Figs.35 and 36). Surface NCa mixes conservatively with increasing NCa when salinity decreases. Subsurface water has the opposite trend of surface water: NCa increase with increasing salinity. However, the difference of overall deep water NCa of ENP and WNP seems too large to account for the difference of NTA of the two sets of data. Considering the subsurface samples, ENP has higher NTA than WNP's NTA by about 30 μeq/kg. If only CaCO₃ dissolution is assumed to cause this difference, then the upper limit of difference in NCa should be 15 μmol/kg. However, the observed difference seems to exceed 25 μmol/kg for NCa data. The possibility of systematic error between the two sets of calcium data may not be eliminated. In the 35°N cross-section of Shiller and Gieskes (1980) there is no significant difference in calcium
Fig. 37 Correlation of S with NCa for WNP stations (Data from Feely, 1982).
Fig. 38 Correlation of $\theta$ with NCa for WNP stations. The triangles represent surface data and squares represent salinity minimum data (Data from Feely, 1982).
concentration between the Eastern North Pacific Ocean and the Western North Pacific Ocean.

4.A.(e) Nutrient data:

It has long been known that the oxygen minimum water originates in the deep water of the northern North Pacific and is associated with nutrient maximum (Sverdrup et al., 1942). Figs. 39 and 40 show the vertical distribution of nitrate and phosphate respectively along the 150°W section. Both figures show a maximum core, the axis of which is centered at about 1000 m. The isopleths of both nitrate and phosphate in the surface layer deepen at the mid-latitude and shallow at the high-latitude and at the equatorial region. Silicate, however, is not so uniformly associated with oxygen as the other nutrients. The maximum does not appear on this section (Fig. 41). It is located below the oxygen minimum and is quite broad with values only slightly less than the maximum found just above the bottom. This is shown quite well on plates 13 and 29 of the GEOSECS Pacific Atlas (Craig et al., 1981). The east-west vertical sections along 35°N (Kenyon, 1983) show the silicate maximum at 150°W is at about 2500 m whereas the oxygen minimum is at about 1000 m and the nutrient of both phosphate and nitrate are near 1000 m. Between ENP13 and ENP14, the silicate signal marked by a depression of the isopleths extends from the
Fig. 39 Distribution of NO₃ with depth along the 150°W cross-section (Data from Feely, 1981).
Fig. 40  Distribution of PO$_4$ with depth along the 150°W cross-section (Data from Feely, 1981).
Fig. 41 Distribution of $\text{SiO}_2$ with depth along the $150^\circ\text{W}$ cross-section (Data from Feely, 1981).
surface to the deepest sampling levels. A similar feature was noted at these stations for temperature and salinity but not to the depths indicated by silicate. Were it not for these two stations the general trend of the isopleths would be relatively flat and quite different from the AOU trend which roughly shows a concave downward bow to the isopleths. North of these two stations the silicate values are higher along a particular isopycnal than south of these stations.

Figs. 42-44 show the vertical distribution of nitrate, phosphate and silicate of WNP data. Again, a tongue-like high nitrate and phosphate core, lying at the AOU maximum layer, extends from north to south. The transition from subarctic to subtropic region is marked by surface nutrients. From salinity cross-section (Fig. 4), the subarctic front is lying between WNP14 and WNP16. Across this front, from WNP16 to WNP14, phosphate decreases from 0.85 to 0.10, nitrate from 9.3 to 1.1, and silicate from 17.42 to 4.3 μmol/kg respectively. This characteristic is consistent with the finding of Park (1968c). Like the ENP section, the WNP cross-section of silicate shows a different pattern with an increasing trend with depth, and it does not show a maximum core at the AOU maximum core. Again, this is not surprising because silicate is not remineralized along with the organic matter (Edmond, 1974).
Fig. 42 Distribution of NO₃ with depth along the 165°E cross-section (Data from Cline, 1982).
Fig. 43 Distribution of PO₄ with depth along the 165°E cross-section (Data from Cline, 1982).
Fig. 44 Distribution of SiO$_2$ with depth along the 165°E cross-section (Data from Cline, 1982).
4.B. Alkalinity-Calcium relationship:

The similar pattern between the $\theta$-NTA/$\theta$-NCa and $S$-NTA/$S$-NCa presented in previous sections is not surprising since both calcium and alkalinity are related to the dissolution of $\text{CaCO}_3$ mineral. Several researchers have paid attention to the correlation between these two parameters (Tsunogai et al., 1973; Horibe et al., 1974; Brewer et al., 1975; Shiller and Gieskes, 1980; Tsunogai and Watanabe, 1981; Kanamori and Ikegami, 1982; Ikegami and Kanamori, 1983). Tsunogai et al. (1973) used calcium and alkalinity data of KH70-1 and KH70-2 to study the TA-CA relationship along $170^\circ W$. They found $(2\text{TA-Ca})/\text{Cl}$ is not constant and proposed a possibility of sources of calcium other than the dissolution of calcium carbonate. Horibe et al. (1974) found a correlation coefficient between NCa and Normalized carbonate alkalinity to be about 0.5. Brewer et al. (1975) used surface alkalinity and calcium as a reference and correlated the difference of calcium and alkalinity between measured values and surface reference values (both were normalized to $35\times10^{-3}$ salinity). They found the slope is larger than the theoretical 0.5 slope and proposed potential alkalinity to compensate the effect caused by decomposition of organic matter to the titration alkalinity. Tsunogai and
Watanabe (1981) applied this model to KH78-3, and KH-75-4 data in the northern North Pacific and Bering Sea and received a slope close to 0.5. Kanamori and Ikegami (1982) and Ikegami and Kanamori (1983) used nitrate concentration as an index of the effect of organic decomposition to alkalinity (PA=TA+1.26NO₃) to correlate their KH80-2 and KH82-1 data obtained from the western North Pacific. They also obtained a slope of 0.5 between NCa and normalized PA. In our study, both the nutrients and oxygen are used as an index for the purpose of estimating the organic decomposition effect to the titration alkalinity.

Fig. 45 shows the correlation of NTA and NCA for all the ENP sample. Unlike Tsunogai and Watanabe's (1981) results, the surface data of our ENP stations scattered. NTA/NCa scattering near surface is probably real because the data covered a large area. Shiller and Gieskes (1980) also found a large variation of NCa/NTA ratio from 0.4-0.8 for the INDOPAC mixed-layer samples. Hence, the assumption that preformed calcium value for the surface water and subsurface water is similar, which is suggested by Tsunogai and Watanabe (1981), should be studied further. The least square method is used to fit data points below 200 m depth for the ENP data. However, the NTA/NCa correlation has no physical meaning. The NTA/NCa correlation consists of variation in
Fig. 45 Correlation of NCa with NTA for the ENP data. The regression line shown in the figure is NCA=8996+0.520xNTA for the samples below 200 m.
preformed NTA and NCa which may not be entirely related to CaCO₃ dissolution. The correlation slope is 0.520 ± 0.007 for NTA-NCA correlation. The number, 0.007, represents the range of the slope at the 95% confidence interval. Our slope, 0.520, is much lower than that observed by Horibe et al. (0.734), Brewer et al. (0.688), and Tsunogai et al. (0.74).

Fig.46 correlates normalized potential alkalinity \( [\text{NPTA}_1 = (\text{TA} + \text{NO}_3 + \text{PO}_4) \times 35/8] \) and NCa for the ENP samples. The correlation coefficient for the samples below 200 m is 0.442 ± 0.042. The number, 0.042, represents the range of the slope at 95% confidence interval. The potential alkalinity proposed by Brewer et al. (1975) cannot be confirmed from our data since both of the correlation slopes of NCa-NTA and NCa-NPTA1 do not agree with the theoretical value of 0.5 within the limit of uncertainty. Although we know the protonation due to the organic decomposition on the titration alkalinity plays an important role, the amount of alkalinity that is changed by this protonation is not known. As pointed out by Brewer et al. (1975), the preformed values for nitrate and phosphate were ignored in the potential alkalinity model, which means an overestimated potential alkalinity may be obtained.

Instead of nutrient data, AOU may serve as a better
Fig. 46 Correlation of NCa with NPTAI\[=(TA+NO_3+PO_4)x35/S]\] for the ENP data. The regression line shown in the figure is NCa=9167+0.442xNPTAl for the samples below 200 m.
index to estimate the degree of protonation from organic matter on the alkalinity. It has been discussed by Chen and Pytkowicz (1979), Chen and Millero (1979), and Chen et al. (1981) that 138 mole of oxygen, assuming Redfield-Ketchum-Richards ratio is correct, will be consumed to decompose 1 mole of organic matter and reduce the alkalinity by 17 eq. The model is followed to calculate preformed alkalinity. The normalized potential alkalinity obtained by AOU correction \[ \text{NPTA}_2 = (\text{TA}+17/138) \times \text{AOU} \times 35/S \] is plotted against NCa. The result is shown in Fig. 47. A little improvement is obtained compared to NPTAl-NCa correlation. The least square fit for the samples below 200 m shows the correlation slope being $0.456 \pm 0.042$. The number, 0.042, represents the range of the slope at 95% confidence interval.

In summary, variation of the preformed calcium and alkalinity concentrations needs to be considered in order to properly investigate the influences of CaCO$_3$ dissolution and organic matter decomposition on the measured calcium and alkalinity values. This calls for accurate calcium and alkalinity data in the formation region of the subsurface waters.
Fig. 47 Correlation of NCa with NPTA2 \[= (TA+17xAOU/138)x35/S \] for the ENP data. The regression line shown in the figure is NCa = 9137 + 0.456xNPTA2 for the samples below 200 m.
4.C. Inorganic Carbon/Organic Carbon ratio:

Li et al. (1969) studied the sources of the excess CO$_2$ in the deep water of the Pacific and Atlantic Oceans. They concluded that about 20% of the excess CO$_2$ in the deep water is derived from the inorganic CaCO$_3$ dissolution. Edmond (1974) used a ratio of shell-derived to tissue-derived CO$_2$ in the deep water, without eliminating the effect of fossil fuel CO$_2$ increase, to study the mechanism of TCO$_2$ input. Chen et al. (1981) improved the method of Edmond's (1974) model to calculate inorganic carbon/organic carbon ratio of the South Pacific. They reached the result that about 12% of the total CO$_2$ input into the deep waters of the South Pacific is contributed from CaCO$_3$ dissolution. The same technique is adopted from Chen et al. (1981) but new preformed equations for TA and TCO$_2$ are used. The preformed equations used here are obtained from revised GEOSECS data (Takahashi et al., 1980). The preformed equations will be discussed in the section on fossil fuel CO$_2$ signal. Only the resulting equations are shown here.

\[
\begin{align*}
TA^0(\text{meq/kg}) &= 2384 - 4.2x9 (\pm 9) \\
TCO^0_2(\text{umol/kg}) &= 2219 - 11x9 (\pm 16)
\end{align*}
\]

The inorganic carbon/organic carbon ratio is represented by IC/OC and it was calculated by the following equations:
IC/OC = \[0.16038(\Delta TC_{O2+40}) + \Delta TA\]/[2(\Delta TC_{O2+40}) - \Delta TA]\]

where \(\Delta TC_{O2} = TC_{O2\text{measured}} - TC_{O2}xS/35\)

\(\Delta TA = TA\text{measured} - TA_0xS/35\)

The estimated amount of anthropogenic fossil fuel CO2 signals is 40 \(\mu\text{mol/kg}\) total CO2. Chen et al. (1981) pointed out the importance of the contribution of the fossil fuel CO2 for the IC/OC ratio. Here we use 40 \(\mu\text{mol/kg}\) as the anthropogenic fossil fuel CO2 contribution to the preformed value of TC\(_{O2}\). An underestimate of 0.05-0.07 in IC/OC ratio will be observed if the fossil fuel signal is ignored in calculation. Several GS stations which are close to our two cross-sections are also used to calculated IC/OC ratio. The results are consistent between the data sets.

The distribution of IC/OC with depth for the samples below 500 m is shown in Fig. 48 for ENP, WNP, and selected GS stations. Unlike the South Pacific, there is no sharp decrease in the bottom layer. This is expected because of the Benthic Front (Craig et al., 1972) does not extend into the North Pacific Ocean. The IC/OC ratio increases markedly from 0.1 to 0.35 from 500 m to 2500 m. The IC/OC ratio shows a constant value below 2500 m. This reflects the high degradation rates of organic tissue in upper water. Edmond (1974) found a ratio of 0.26 at a water depth of 3000 m in the Northeast Pacific, which is lower than our value of
Fig. 48 Vertical Distribution of inorganic carbon/organic carbon (IC/OC) ratio for ENP (a) and WNP (b) data.
0.35. From the discussion above, we can conclude that about 25% increase in TCO₂, after leaving from the Southern Ocean, is contributed by inorganic CaCO₃ dissolution below a water depth of 3000 m.

Figs. 49 and 50 show the different ways to express the distribution of IC/OC ratio. The solid lines represent the value of IC/OC. The dashed lines represent contours of total input of TCO₂ since the water mass leaves its source region. Since oxidation of organisms contributes the largest part of TCO₂ increase (about 75% for deep water), the layer of maximum increase of TCO₂ is generally coincident with the maximum AOU layer. Two southernmost stations of both the ENP and WNP cruises (ENP16,19, WNP3,5) show the lowest extreme of TCO₂ increase, which is a result of less influence from the oldest NPDW.

It is also found that ENP stations have higher total TCO₂ input than that of the WNP cruise. This is expected due to the fact of the older age of the Northeast Pacific Deep Water. ENP stations show a narrower range of increase and a higher increase of TCO₂ than the WNP stations for the deep water, which means more homogeneous water was found in the Eastern North Pacific. WNP18 and WNP20 have unique characteristics (Fig. 50). First, they have a lower IC/OC ratio at the same isopycnal surface than the other stations.
Fig. 49 Correlation of IC with OC for the ENP data. Dashed lines represent the total input of TCO$_2$ (=IC+OC).
Fig. 50 Correlation of IC with OC for the WNP data. Dashed lines represent the total input of TCO₂ (=IC+OC).
This lower IC/OC ratio is a consequence of lower inorganic CaCO$_3$ input to TCO$_2$ and/or higher input from organic decomposition. Second, WNP20 has a thick layer of high TCO$_2$ increase. This is the result of high CO$_2$ content water which was pumped up to the surface layer through upwelling. We cannot find an analogous station from the ENP cruise.

The maximum IC is always found lying below the depth of OC maximum. The IC part of TCO$_2$ increase does not show a significant increasing trend after IC maximum is achieved. This could be explained by kinetic control on the dissolution of CaCO$_3$ minerals. Edmond (1974) also postulated that the calcareous tests are transported as far as the deep water before significant dissolution takes place.
4.D. Degree of saturation of CaCO$_3$, lysocline, and CCD

It is well-known that the deep water of the North Pacific Ocean represents the oldest age of the world oceans. Hence, the concentration of carbonate ion in the North Pacific Ocean shows the lowest value. Takahashi et al. (1981) found a low mean CO$_3^{2-}$ concentration in the Pacific Ocean and attributed this to the low alkalinity/total CO$_2$ ratio of this area. The result of low CO$_3^{2-}$ concentration is a lower degree of saturation and then a shallower saturation horizon of the Pacific Ocean than the other regions.

The distribution of the saturation value of seawater with respect to calcite and aragonite will be presented and its relationship with compensation depth and lysocline will be addressed.

4.D.(a) Method of calculation of degree of saturation:

In calculation of degree of saturation of seawater with respect to calcite and aragonite, the carbonate ion concentration has to be calculated from the measured carbonate data. The CO$_3^{2-}$ concentration in seawater at the in situ temperature and pressure conditions has been computed using the WNP's and ENP's salinity, temperature, alkalinity, pH, and calcium data. In addition to our two meridional sections along 165°E and 150°W, all the GEOSECS and INDOPAC
alkalinity and total CO2 of the North Pacific Ocean are used to calculate the degree of saturation of seawater. Two cross-sections, one longitudinal along roughly 180° and one latitudinal along roughly 35°N, are selected from GEOSECS stations to make the distribution of saturation value clearer. The effect of pressure on the dissociation constants for carbonic and boric acids determined by Culberson et al. (1967) and Culberson (1972) is used for the computation. Our expression for the saturation states for calcite and aragonite in seawater is in percent of saturation:

$$\Omega = \frac{ICP}{K'sp} \times 100\%$$

where $$ICP = (Ca^{+2})(CO_3^-)^2 (M/kg)^2$$.

$$K'sp$$ = apparent solubility product for calcite or aragonite

The apparent solubility product for calcite and aragonite in seawater at 1 atm total pressure determined by Ingle et al. (1973) and by Berner (1976), respectively, are used. In order to obtain the apparent solubility product at in situ conditions, the pressure effect on the solubility products summarized by Culberson (1972) is used.

4.D.(b) Degree of saturation of the surface water:

Figs. 51 and 52 show the correlation of temperature with
Fig. 51 Correlation of surface $\Omega_c$ with temperature for all available data. The line is a rough fit by eyes.
Fig. 52 Correlation of surface $\Omega_a$ with temperature for all the available data. The line is a rough fit by eyes.
degree of saturation of seawater with respect to calcite ($\Omega_c$) and aragonite ($\Omega_a$), respectively, for the surface water of the North Pacific Ocean. It is evident that all the surface waters are CaCO$_3$ oversaturated. The linear correlation between $\Omega_c$, $\Omega_a$ and temperature is found in both figures. A high degree of saturation is observed for high temperature surface seawater and a low degree of saturation is observed for low temperature surface seawater. This is consistent with the work of Lyakhin (1968) who studied the calcium carbonate saturation of Pacific water.

The degree of saturation value is strongly influenced by TA/TCO$_2$ ratio which also shows a linear dependence to the surface temperature.

The contours of the surface saturation value are constructed in Figs. 53 and 54 for calcite and aragonite, respectively. The overall pattern is similar to the temperature distribution which in turn is influenced by the surface oceanographic circulation. $\Omega_c$ and $\Omega_a$ decrease slightly from west to east. In western subarctic regions low $\Omega_c$ and low $\Omega_a$ are observed which are the characteristics of the cold Oyashio current. Low $\Omega_c$ and low $\Omega_a$ are also found in cold Gulf of Alaska. A sharp change from north to south at the region of mixing between the cold Oyashio and warm Kuroshio around 40°N occurred. A high $\Omega_c$ and $\Omega_a$ basin
Fig. 53 Distribution of surface $\Omega_c$ in the North Pacific Ocean.
Fig. 54 Distribution of surface $\Omega_a$ in the North Pacific Ocean.
at the center of the subtropical region is not clear enough to be defined.

4.D.(c) Vertical distribution of degree of saturation:

Four cross-sections of saturation values of calcite and aragonite are plotted by using the ENP, WNP, and GEOSECS data. The selected longitudinal and latitudinal sections are shown in the map (Fig. 1).

(1) Profile along 35°N:

The latitudinal cross-section along approximately 35°N was selected also by Takahashi (1975). But non-adjusted TCO₂ data was used to calculate saturation value and only the Qₐ was calculated in his paper. The revised carbonate data (Takahashi et al., 1980) is used to recalculate the degree of saturation of both calcite and aragonite. The results are shown in Figs. 55 and 56. A very small variation of saturation value is found in the water column below 1000 m depth. A shoaling phenomenon of the saturation horizon from the west to the east, is caused by the general surface circulation pattern in the North Pacific Ocean. The west North Pacific has the deepest saturation horizon at a depth of 1100 m. The intensified western boundary current results in the deepening of the saturation horizon. A characteristic minimum Qₐ and Qₐ layer can be seen all the way from coast to coast. This minimum layer is relatively narrow and was
Fig. 55 Vertical distribution of $\Omega_c$ along the 35°N cross-section. Dashed line represents CCD from Berger et al. (1976).
Fig. 56  Vertical distribution of $\Omega_a$ along the 35°N cross-section.
not shown in Takahashi's (1975) profile. The existence of this layer is strongly related to the oxygen minimum layer. The low saturation value found in this layer is believed to be caused by high oxidation of organic matter, which releases the carbon dioxide and reduces the carbonate ion concentration.

(2) Profile along 165°E:

Fig. 57 shows distribution of the saturation value of calcite along 165°E. The saturation horizon deepens from less than 150 m at the north to deeper than 3000 m at 25°N. Fig. 58 shows the saturation horizon of aragonite onset from less than 100 m at north, from 750 m at 30°N, and from 500 m at 15°N. Byrne et al. (1984) studied the dissolution rate of aragonite particulates collected by free-drifting sediment trap along the Discoverer cruise. Their findings revealed that the depth at which high dissolution rate of aragonite was found is shallower at high latitude than that of at mid-latitude. This is a support of our saturation profile which shows that the saturation horizon concaves at mid-latitude.

A sharp change from undersaturation to supersaturation for calcite is found in between WNP5 and WNP6. The oversaturated water at WNP3 and WNP5 may be the result of the younger age of the seawater at that region. WNP6 defined the southern limit of NPDW which is low oxygen, high
Fig. 57  Vertical distribution of $\Omega_c$ along the 165°E cross-section.
Fig. 58  Vertical distribution of $\Omega_a$ along the 165°E cross-section.
nutrients, and acidic water. Such a sharp change of saturation value from north to south was also observed by Hawley and Pytkowicz (1969) along their 170°W cross-section. We do not have deep enough samples at WNP3 and WNPS to see the distribution of saturation value down to the bottom. A core of low saturation value is found as a tongue extending from north to south at a water depth of 700 m.

It is clear that the saturation horizon is also affected by the surface circulation. A depression of saturation contours at 30°N is located slightly south of the subtropical convergence zone. The contour line of saturation horizon almost outcrops to the surface at 50°N. Again, an upwelling must play an important role on this shallow saturation horizon.

(3) Profile along 180°W:

Takahashi (1975) selected similar but not identical cross-sections. Only a calcite saturation value was calculated from the original GEOSECS data set in his paper. As the 165°E cross-section, the contour lines in the surface layer concave downward at mid-latitude (Figs. 59 and 60). The 100% Ωc contour and 70% Ωa contour deepen from 300 m at the north to 2200 m at the south. Such a trend may depict the large scale upwelling phenomenon for the deep water of the northern region. The cores of low saturation value are observed in both Figs. 59 and 60. Takahashi (1975) did not
Fig. 59 Vertical distribution of $\Omega_c$ along the 180° cross-section. Dashed line represents CCD from Berger et al. (1976).
Vertical distribution of $\Omega_a$ along the 180° cross-section.
show this minimum core in his paper.

(4) Profile along 150°W:

This data set was presented by Feely and Chen (1982) who used the estimated calcium concentration to calculate the ionic product for the data above 1500 m. Figs. 61 and 62 show our results of recalculated saturation value using measured calcium concentration for all the samples taken. The distribution pattern is similar to the profile along 165°E.

4.D.(d) The relationship among $\Omega_c$, lysocline, and CCD:

The mechanisms that control the distribution of the calcium carbonate sediments is not clear. The relationship among the saturation horizon, lysocline, and calcium carbonate compensation depth (CCD) has been investigated by several workers (Li et al., 1969; Edmond and Gieskes, 1970; Pytkowicz, 1970; Heath and Culberson, 1970; Lisitzin, 1972; Takahashi, 1975; Broecker and Takahashi, 1978). In order to examine the above mentioned three properties, we need to know the distribution of saturation horizon, lysocline, and CCD. Peterson (1966) and Berger (1967) carried out in situ experiments of the dissolution of calcite in the Central North Pacific Ocean (18°49'N 168°31'W). Their work has contributed knowledge to the in situ carbonate dissolution study. It was found that at a depth of about 3700 m the rate of dissolution of calcite increases sharply. The depth is
Fig. 61 Vertical distribution of $\Omega_c$ along the 150°W cross-section.
Fig. 62 Vertical distribution of $\Omega_A$ along the 150°W cross-section.
called lysocline. Unfortunately, this kind of experiment is scarce for the study to be more extensive. Another indirect approach of lysocline was carried in laboratory experiments by Morse and Berner (1972) and Berner and Morse (1974) by examining the parameter, ΔpH, the difference between the pH value for the calcite-seawater equilibrium and that of seawater pH value. Takahashi (1975) suggested a ΔpH value of 0.08 instead of 0.15 proposed by Morse and Berner (1972) as an indicator of a sharp increase dissolution rate of calcium carbonate. According to Berner and Wilde (1972), ΔpH=0.08 is equal to the saturation value of 91% \( \Omega_c \). This value is adopted in this thesis as a qualitative reference of lysocline depth. The term "qualitative" is carefully used because of the vague depth at which \( \Omega_c = 91\% \) falls. A large amount of water in the North Pacific has a calcite saturation value of 90-100\% \( \Omega_c \). The scattering of data also contributes a large enough noise for the \( \Omega_c = 91\% \) depth to be poorly defined.

In Figs. 55 and 59 the CCD is shown according to the work of Berger et al. (1976). It can be seen that CCD usually falls on a depth above the 80\% \( \Omega_c \) contour in the mid-latitude region. Fig. 59 shows a shoaling of CCD north of 40\°N to a depth where the \( \Omega_c \) value is larger than 90\%. If 90\% \( \Omega_c \) contour was defined as lysocline in the North Pacific, then CCD generally falls on a depth deeper than
lysocline and lysocline generally falls on a depth deeper than the saturation horizon of calcite.

GS233 is selected for the purpose of discussion of the relationship between $\Omega_c$, lysocline, and CCD. This station is selected because it is located near the station at which Peterson's (1966) in situ experiment was carried out. The distribution of carbonate ion concentration and normalized alkalinity at GS233 is also shown in Fig.63 down the water column from surface to sea bottom. Even though the maximum uncertainty of determination of the saturation horizon, 750 m, is considered (Plath et al. 1980; Pytkowicz, 1983) the depth is still much shallower than lysocline and CCD depth. The depth of lysocline estimated from $\Delta p$H is consistent with Peterson's (1966) at a depth of about 3500 m. Berger et al.'s (1976) CCD at about 4400 m is also shown in the figure. The difference of depths of saturation horizon, lysocline, and CCD cannot be explained except by kinetic arguments.

$\text{CO}_3^{2-}$ concentration increases slightly below a depth of saturation horizon. However, this increase cannot be attributed only to the dissolution of CaCO$_3$. Not only CaCO$_3$ dissolution but also the effect of physical condition and pH value on the speciation of carbonic acid affect the concentration of $\text{CO}_3^{2-}$ ion. Nevertheless, the general increasing trend of $\text{CO}_3^{2-}$ concentration and decreasing trend
Fig. 63 Vertical distribution of $\Omega_c$, $CO_3^-$, and NTA at CS233.
of saturation value below the saturation horizon still give
the inference of the importance of solubility product on the
saturation value for the deep water.

NTA is independent of temperature, salinity, and
pressure effect if per weight unit was used. Hence, NTA
distribution may serve as a better indicator of CaCO₃
dissolution than CO₃⁻ ion concentration. The significance of
a maximum NTA layer is noted here. The maximum NTA layer
generally lying at a depth between 3000-3500 m in the North
Pacific is always shallower than both lysocline and CCD.
This is not expected since the deep lysocline and CCD should
imply more CaCO₃ dissolution below these depths, hence, an
increasing trend should be found. The explanation for this
phenomenon is that the rate of dissolution of CaCO₃ is not
fast enough to overcome the flushing of bottom water at that
region. The location of GS233 is one of the main passages of
the Pacific Bottom Water with relatively high current speed
of about 10 cm/sec originated from the Southern Ocean
(Edmond et al., 1971). The rate of delivery of low
alkalinity bottom water is higher than the rate of in situ
production from dissolution of CaCO₃.
4.E. Anthropogenic fossil fuel CO₂ signal:

4.E.(a) Method of calculation:

The method of computation and limitation of the model have been described in detail elsewhere (Chen and Pytkowicz, 1979; Chen and Millero, 1979; Chen, Millero and Pytkowicz, 1982). The following equations summarize the method.

\[
\text{excess CO}_2 = \text{TCO}_2^O(\text{present}) - \text{TCO}_2^O(\text{old})
\]

\[
= \text{TCO}_2^O(\text{present}) - \text{TCO}_2(\text{measured}) - 0.5 \\
\text{TA}(\text{measured}) - 0.78 \text{ AOU} + 0.5 \text{ TA}^O(\text{present})
\]

where all quantities except AOU are normalized to 35x10⁻³ salinity.

Since the old deep water are free from the fossil fuel CO₂, the TCO₂ for the deep water must be smaller than the TCO₂ of the young surface water from which the preformed equation is derived. Hence, the excess CO₂ for the deep water has a positive value while the excess CO₂ for the surface water is zero.

In the various mathematical terms of the above equation the preformed equations of alkalinity and total CO₂ (TA and TCO₂) and the coefficient preceding the AOU are most controversial. Hence the discussion of these quantities will be emphasized before the results of calculation are presented.

4.E.(b) Preformed equations and AOU coefficients:
The main idea of the model proposed by Chen and Millero (1979) is: the difference between the TCO$_2$ of the anthropogenic CO$_2$ free seawater and the TCO$_2$ of its source seawater which contains the full amount of anthropogenic CO$_2$ reflects the increase of excess CO$_2$. How to select a proper preformed value for TA and TCO$_2$ to calculate excess CO$_2$ is one of the most problematic parts of this model. To attack this problem the GS data has been used to derive the preformed equations (Chen and Pytkowicz, 1979). Instead of using all the surface NTA and NTCO$_2$ of the GS expedition, it is more suitable to use the surface NTA and NTCO$_2$ of those waters representing the source of the water under study. It has been accepted long before that the Southern Ocean are the only source of deep waters in the Pacific (Sverdrup et al., 1942; Knauss, 1962). Hence, surface NTA and NTCO$_2$ for those GS stations south of 50°S are used to derive the preformed equations. Fig.64 shows the correlation of surface NTA and NTCO$_2$ with temperature for those GS stations located south of 50°S. These stations encompassed all three large oceans in the southern region. The reason for adding some stations north of the Antarctic Convergence is to increase the sample size which covers a wider range of temperature to get a more reliable regression line. The least-squares fit of these data result in the following equations:
Fig. 64 Correlation of surface NTA and NTCO$_2$ with temperature for the GS data in the Southern Ocean.
Both \( \text{TA}^\circ \) and \( \text{TCO}_2^\circ \) are normalized to 35x10^{-3} salinity and the numbers in parentheses give one standard deviation of the fit for the above equations. These equations are used to calculate excess CO\(_2\) for the water below NPIW. For the water above NPIW the situation is very complicated because the suitable preformed TA and TCO\(_2\) cannot be found from existing data. The surface TCO\(_2\) in the North Pacific Ocean is very complicated. As presented in Fig.65 different trends can be found depending on the geographical location of the stations. In Fig.65 the surface NTA and NTCO\(_2\) are denoted by different symbols depending on the location of the stations in the North Pacific Ocean. Fig.65(a) shows all the \( \theta \)-NTA correlation falls on one linear line. The linear fit for these data is NTA=2407-3.46x\( \theta \). Hence, the preformed alkalinity of the North Pacific surface water is always larger than that of the deep water in the range of temperature found in the world oceans. Fig.65(b) shows the correlation of surface NTCO\(_2\) with temperature for the North Pacific GS stations. Unlike \( \theta \)-NTA correlation, three groups of data – Northwest Pacific, equatorial, and other stations – can be recognized. None of these trends is coincident with the preformed TCO\(_2\) equation derived from the Southern Ocean.
Fig. 65 Correlation of surface NTA and NT\textsubscript{CO}_2 with temperature for the GS data in the North Pacific Ocean. The triangles represent GS stations located in the Northwest North Pacific. The crosses represent GS stations located in the equatorial regions. The solid dots represent the others.
data. The cause of these different trends is not known. The NTCO$_2$ at certain temperatures is different for the samples found in the different area, especially for high temperature data. This difference is too large to get a unique preformed total CO$_2$ equation. Such a different surface $\Theta$/NTA and $\Theta$/NTCO$_2$ correlation between the North Pacific and Southern Ocean leads to the conclusion that the preformed NTA and preformed NTCO$_2$ of the surface layer and the deep layer must be different. If this is true, a mixing problem will arise. It is feasible to use its own preformed equations for the surface mixed layer. However, it is difficult to determine the preformed TA and TCO$_2$ value for those waters that are subject to mixing from different water masses if the mixing ratio is unknown. For NPIW it is even more complicated because the surface NTA and NTCO$_2$ in the northwestern North Pacific Ocean where the NPIW originates is not available. However, we can say that the surface excess CO$_2$ should be zero. Through extrapolation and data examination it is still possible to see the fossil fuel signal in the North Pacific Ocean.

The equation for calculating the excess CO$_2$ mentioned above is rearranged:

$$[\text{TCO}_2^0(\text{present}) - \text{TCO}_2(\text{measured})] - 0.5 [\text{TA}(\text{measured}) - \text{TA}_0^0(\text{present})] = 0.78 \text{ AOU} + \text{excess CO}_2$$
\[ \Delta T CO_2 - 0.5 \Delta TA = 0.78 \text{ AOU} + \text{excess CO}_2 \]

Hence, if \((\Delta T CO_2 - 0.5 \Delta TA)\) is plotted against AOU a slope of 0.78 should be obtained and the intercept is the fossil fuel CO\(_2\) increase signal. This has been done by Chen and Pytkowicz (1979). By using the same stations in their paper and newly derived preformed equations \((\Delta T CO_2 - 0.5 \Delta TA)\) is recalculated and plotted against AOU for the sample below the AOU maximum layer. The result is shown in Fig. 66. The correlation slope is 0.78 and the intercept is \(-40 \mu\text{mol/kg}\).

4.E.(c) Penetration depth along 150\(^\circ\)W and 165\(^\circ\)E sections:

Figs. 67 and 68 show the results of fossil fuel CO\(_2\) penetration along the 150\(^\circ\)W and 165\(^\circ\)E cross-section. The waters underlying the 40 \(\mu\text{mol/kg}\) excess CO\(_2\) contour have a homogeneous excess CO\(_2\) value close to 40 \(\mu\text{mol/kg}\), which means these waters are free from fossil fuel CO\(_2\). The decreasing excess CO\(_2\) from deep to surface layer means more fossil fuel CO\(_2\) content in the shallow water than in the deep water. Chen (1982) has discussed the penetration of excess CO\(_2\) along the ENP section. He proposed that the deepening of penetration depth at 30\(^\circ\)N (Fig. 67) is not a local phenomenon but is an advected feature derived from the northwest North Pacific. The WNP section, 50\(^\circ\) west of the
Fig. 66 Correlation of \([0.5\Delta TA + \Delta TCO_2]\) with AOU for deep water of the selected GS Pacific stations.
Fig. 67 Distribution of excess CO$_2$ along the 150°W cross-section (taken from Chen, 1982).
Fig. 68 Distribution of Excess CO$_2$ along the 165°E cross-section.
ENP, shows a similar form as the ENP section but with generally deeper penetration depth. The shoaling penetration from west to east is also seen in tritium distributions which are also supported by recent atmospheric inputs. Fig. 69 shows the east-west vertical section along 35°N of tritium reproduced from Fine, Reid, and Ostlund (1981). The 0.5 TU contour shoals from 900 m at 165°E to 600 m at 150°W. The zero TU was not shown in their figure. If the zero TU contour is assumed to be parallel to 100 m underlying 0.5 TU contour, then the penetration depth from tritium data is 1000 m at 165°E and 700 m at 150°W. This result is very consistent with our results for excess CO₂ (Figs. 67 and 68).

Fig. 70 shows the vertical section of tritium, also reproduced from Fine et al. (1981), from selected GS stations between 15°-55°N between 165°W and 170°E (see Fig. 1). This section is located between our two sections. Similar to our excess CO₂ pattern, the 0.2 TU contour shows an overall concave structure with the deepest penetration at 900 m or deeper at 38°N and the shallowest penetration at 400 m at 10°N. It is significant to note that the tritium data shown here are from the GEOSECS expedition which occurred about ten years earlier than our ENP and WNP expedition. Therefore, the penetration depth obtained from
Fig. 69 Distribution of tritium along the 35°N. This figure is reproduced from Fine et al. (1981).
Fig. 70  Distribution of tritium at selected GS stations extending from 15° to 55°N between 165°W and 170°E (see Fig. 1). This figure is reproduced from Fine et al. (1981).
the tritium data shown here may be shallower than today's depth of penetration since vertical diffusion and continued advecion are still bringing the fossil fuel CO$_2$ signal downward over the last decade. An increasing penetration depth of tritium has been observed in several regions of the world oceans (Broecker and Peng, 1982). Sarmiento (1983a,b), using tritium data from the North Atlantic, estimates that penetration along isopycnals to depths of 700 m may occur rapidly, on the order of 10-40 years, and that deeper penetration occurs on a longer time scale. Jenkins (1980, 1982) also finds renewal rates to be on a decade scale for the Sargasso Sea using $^3$He and tritium.

In Fig. 68 the deepest excess CO$_2$ signal can be found at a depth of 1500 m ($\delta_e=27.5$) at 25-30°N where the contours of the other physical and chemical properties also concave downward. The 40 $\mu$mol/kg contour north of about 40°N shows a deeper penetration which is in contrast to the upwelling phenomenon proposed in previous sections since upwelling should bring the older subsurface water to the upper layer. There is a possibility that the excess CO$_2$ signal found in this layer is attributed to the NPIW which originates from its aeration source area (see 3.8 for the discussion of the NPIW). In other words, it is possible that there is some source for this water mass that is not of Southern Ocean
origin. This cannot be proven unless more information is available in the northwest North Pacific Ocean. A dashed line is drawn for the northern end of 40 µmol/kg contour to show the uncertainty of the excess CO₂ distribution.

4.E.(d) Penetration depth in the North Pacific Ocean:

The calculation of excess CO₂ is subject to relatively large uncertainty from various sources (Chen and Millero, 1979) and effects the accuracy of the calculation of the depth of penetration. However, from the more precise data sets we still can qualitatively estimate the penetration pattern in the North Pacific. Fig. 71 shows the estimated penetration depth in the North Pacific Ocean by using all the available data sets. The overall pattern shows a similarity with the oceanographic feature. The penetration depth is generally deeper for those areas of high advection and is shallower for more stagnant regions and upwelling areas.

Several prominent features can be found: (1) A general shoaling trend from west to east is observed; (2) a deepening of penetration depth at 35-40°N which is coincident with subtropical convergence; (3) a deep pool at the western North Pacific, away from Japan, is observed. The deepening is probably related to the interaction of Kuroshio
Fig. 7.1 Penetration depth of the fossil fuel CO₂ in the North Pacific Ocean.
and Oyashio currents. The mixing of these currents enhances the penetration of fossil fuel CO$_2$ into the ocean; (4) the penetration depth in the equatorial upwelling region is the shallowest in the North Pacific Ocean. The penetration depth is less than 300 m, especially in the eastern equator area.
5. Conclusions:

With the emphasis on the chemistry in the North Pacific Ocean, the following conclusions can be made:

* NTA, NCa, and silicate show a different distribution than those properties effected by the shallow decomposition of organic matter (AOU, pH, NTCO₂, nitrate, phosphate). They generally increase monotonically with depth. The reason for this is that these substance are released by dissolution, enhanced by pressure, while the soft organic matter is oxidized within the water column. The oxidation occurs primarily in the intermediate waters which bring a large organic load from high latitudes.

* Chemistry data shows that the deep water of the eastern North Pacific is older than that of the western North Pacific.

* Alkalinty data is useful for the water mass analysis. Each water mass shows its own variation trend with temperature.

* Our work of alkalinity-calcium relationship shows that preformed calcium concentration of the surface water may not be the same as that of the subsurface water.

* Our carbonate data analysis shows that about a 25% increase in total inorganic CO₂ of deep water, after
leaving from the Southern Ocean to the North Pacific Ocean, is contributed by inorganic CaCO$_3$ dissolution.

* In comparing the Miller Freeman and Discoverer data, there is no significant difference of IC/OC ratio. However, it was found that the eastern section has higher TCO$_2$ input than that of the western section due to the older age of the deep water along the eastern section.

* The saturation horizon of the North Pacific Ocean with respect to calcite and aragonite generally shallows from the west to the east and from the south to the north. This depth was found at a depth much shallower than that of the lysocline and CCD depth.

* A new set of preformed equation for the excess CO$_2$ calculation for the deep water was obtained from the revised GS data:

\[
\begin{align*}
\text{TA}^0 (\text{µeq/kg}) &= 2384 - 4.2 \times \theta (+9) \\
\text{TCO}_2^O (\text{µmol/kg}) &= 2219 - 11 \times \theta (+16)
\end{align*}
\]

* The penetration depth of fossil fuel CO$_2$ in the North Pacific Ocean was constructed. The penetration depth is influenced not only by the vertical diffusion but also by horizontal advection. Pycnoclines also play a role on the penetration depth in the region where the pycnocline is found. The deepest penetration depth is greater than 2000 m, which is found in the western
North Pacific Ocean. The shallowest penetration depth is less than 300 m, which is found in the eastern equatorial region.
6. References:


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