Descriptive Chemical Oceanography of the Weddell Sea

CHEN-TUNG A. CHEN

Reprinted from Proceedings of the National Science Council
Part A: Physical Science and Engineering
Vol. 15, No. 2, pp. 133-142, March 1991
National Science Council
Taipei, Taiwan
Republic of China
Descriptive Chemical Oceanography of the Weddell Sea

CHEN-TUNG A. CHEN

Institute of Marine Geology
National Sun-Yat Sen University
Taiwan, Kaoshuing, Republic of China

(Received: November 3, 1990; Accepted: December 24, 1990)

ABSTRACT

Concurrent CTD, salinity, O₂, nutrients, pH, calcium, total alkalinity, total CO₂ and pCO₂ were obtained in the Weddell Sea in the late austral winter of 1981 as part of the Weddell Polynya Expedition aboard the Soviet icebreaker SOMOV. These data represent the initial concentrations of chemicals in the most important source region of world ocean bottom waters at the time they were formed. These winter Weddell Sea data were analyzed along with summer data reported in the literature, and the results indicate that: large variations in chemical concentrations occur across the Polar Front; pCO₂ in the Weddell Sea surface water is only slightly lower than the atmospheric value; mixing dominates the distribution of chemical properties; pH, O₂, total CO₂ and pCO₂ are useful in identifying the sources of waters in the Weddell Sea, whereas calcium and alkalinity are not; deep waters are not homogeneous but show discontinuities; the upwelled Weddell Sea Deep Water makes up approximately 1/3 of the surface layer.

Keywords: Weddell Sea, salinity, temperature, oxygen, nitrate, pH, total alkalinity, total CO₂, pCO₂, calcium, Polynya, mixing, C-13, silicate, phosphate

I. Introduction

The three major oceans, the Atlantic, Pacific and Indian, are linked by the Southern Ocean, where free interocean circulation tends to equalize the physical and chemical characteristics of the major oceans. In essence, deep waters from the three oceans flow to the Southern Ocean and mix there. The resultant relatively homogeneous water becomes the major source of the Antarctic Bottom Water (AABW), which spreads back out into the deep world oceans.

The Weddell Sea is considered the major source of the AABW; we must know the chemical constituents of the Weddell Sea water, therefore, in order to understand their biogeochemical cycles from the global point of view. Unfortunately, few extensive geochemical sampling programs have been made in the Weddell Sea (Weiss et al., 1979). As a result, interpreting variations of the geochemical properties of many elements in the deep oceans is difficult, because we do not know the characteristic properties of the water near its origin. Furthermore, the scant geochemical data in the Weddell Sea were all collected in summer, and whether the summer data are representative of the mainly winter-formed deep waters is uncertain (Chen and Pytkowicz, 1979; Chen, 1982a; 1988; Chen et al., 1990).

This work was undertaken as part of the Weddell Polynya Expedition (WEPOLEX) in the late austral winter of 1981. The pH and total alkalinity (TA) of seawater samples were measured aboard ship and seawater samples were collected for shore-based measurements of calcium. The pH and TA data were used to calculate total CO₂ (TCO₂) and CO₂ partial pressure (pCO₂). These data are here combined with CTD, salinity, O₂, nutrients, and C-13 data reported elsewhere (Huber et al., 1983; Kroopnick, 1985) to describe water mass characteristics in the Weddell Sea and nearby regions.

II. Outline of the WEPOLEX Expedition

Concurrent pH, calcium and TA samples were collected on the research vessel, Mikhail Somov, of the Arctic-Antarctic Research Institute (AARI) of Leningrad, USSR. The expedition started in Montevideo, Uruguay, on 9 October 1981, reaching the ice edge near 5°E at 56°30’S on 20 October. The southernmost point was reached at 62°20’S on 3 November. The ship left the ice edge at 57°30’S near the Greenwich Meridian on 14 November and returned to Montevideo on 24 November. The station locations are shown on Fig. 1. Details of the expedition and vertical station locations are given in Chen (1984).
Table 1. Standardization of the pH Electrode and the Inter-calibration of the NBS and Soviet Buffers

<table>
<thead>
<tr>
<th>Buffers</th>
<th>Measured pH</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.004 (NBS)</td>
<td>4.004</td>
<td>(standard)</td>
</tr>
<tr>
<td>4.01 (Soviet)</td>
<td>3.998</td>
<td>-0.012</td>
</tr>
<tr>
<td>6.86 (Soviet)</td>
<td>6.860</td>
<td>0.000</td>
</tr>
<tr>
<td>6.863 (NBS)</td>
<td>6.864</td>
<td>0.001</td>
</tr>
<tr>
<td>7.415 (NBS)</td>
<td>7.415</td>
<td>(standard)</td>
</tr>
<tr>
<td>9.18 (Soviet)</td>
<td>9.187</td>
<td>0.007</td>
</tr>
</tbody>
</table>

The matic difference was found between these two sets of data. All samples were stored in amber plastic bottles, and the alkalinity measurements were accomplished within 12 hours after samples were aboard.

Stored calcium samples were determined using the method of Tsunogai et al. (1968) and Oison and Chen (1981). The precision of the measurements is 5 μ mol/kg, but the overall precision of the Ca data is ±15 μ mol/kg, because some samples were frozen and irreversibly altered (Chen, 1984).

IV. pH, Titration Alkalinity, Total CO₂, Nutrients and CO₂ Partial Pressure in the Surface Water

The values of pH (at 25°C) in surface waters obtained between 12 October and 19 October seemed to decrease as temperature decreased. As the ship moved into the pack ice, the pH values decreased sharply by roughly 0.03 units (Poisson and Chen, 1987). No diurnal pH variability was observed: the pH values of several samples collected at a small polynya (2.0°E, 60°S) on 27 October remained essentially constant for over thirty hours (Fig. 2). The pH value for a stored sample (stored in amber plastic bottles at room temperature) also varied little for four hours (Fig. 2), indicating low bacterial activity. The biological activity for waters below the pack ice was also found to be low (Maira and Boardman, 1984).

The surface water pH values in the ice field remained essentially constant: a total of 82 surface measurements within the pack ice yielded an average pH of 7.851 (1σ = 0.069) at an average temperature of -1.82°C (1σ = 0.091°C). The surface pH values, however, increased sharply again by approximately 0.03 units on 14 November when the ship left the pack ice. In the open ocean the pH values also increased steadily with temperature (Poisson and Chen, 1987). The November pH values are indistinguishable from the October values south of the Polar Front, possibly because the primary
salinity) values seemed to increase steadily with decreasing temperature (Chen and Millero, 1979; Chen and Pytkowicz, 1979), although there seemed to be a smaller change south of the Polar Front. No significant change was detected in and out of the ice field, or between October and November (Poisson and Chen, 1987).

This author calculated the TCO₂ and pCO₂ values using the measured pH and TA values. The contributions of species such as phosphate (PO₄) and silicate (SiO₂) to the alkalinity correction were accounted for. The measured phosphate and silicate values were used when available (Huber et al., 1983); otherwise, these concentrations were calculated according to the following equations based mainly on the GESECS and the Islas Orcadas (Huber et al., 1981) data in the South Atlantic (Chen, 1984; Figs. 3-4).

\[ \text{NPO}_4 = \text{PO}_4 \times 35.0 / \text{salinity} \]

\[ \begin{aligned}
&= 1.7 \mu\text{mol/kg} & T &< 4^\circ\text{C} \\
&= 2.2 - 0.13T \mu\text{mol/kg} & 4^\circ\text{C} &\leq T < 16^\circ\text{C} \\
&= 0.1 \mu\text{mol/kg} & T &> 16^\circ\text{C} \\
\end{aligned} \]

\[ \text{NSiO}_2 = \text{SiO}_2 \times 35.0 / \text{salinity} \]

\[ \begin{aligned}
&= 60 \mu\text{mol/kg} & T &< 2^\circ\text{C} \\
&= 99.4 - 19.7T \mu\text{mol/kg} & 2^\circ\text{C} &\leq T < 5^\circ\text{C} \\
&= 1 \mu\text{mol/kg} & T &> 5^\circ\text{C} \\
\end{aligned} \]

The normalized surface TA (NTA = TA x 35.0/

Fig. 3. Surface NPO₄ values vs. seawater temperature in the South Atlantic Ocean.
rate in November, possibly as a result of primary production in late October and early November. The general circulation around Antarctica is such that the southward-flowing deep waters upwell near the continent, bringing with them high concentrations of alkalinity, total CO$_2$ and nutrients. A portion of the Antarctic surface water then spreads northward away from Antarctica. In the mean time, the surface water being warmed loses alkalinity, total CO$_2$ and nutrients as a result of biological productivity. Higher temperatures may also enhance the formation of CaCO$_3$, either biologically or inorganically, further reducing TA and TCO$_2$. The breaks between 2°C and 4°C in the nutrients/temperature correlations correspond roughly to the region of the Polar Front. Why pH, NTA, NTNT and nutrients should correlate with temperature, however, is not clear. The normalized GEOSECS nitrate values correlate with temperature as follows (Fig. 5):

$$\text{NNO}_3 = \text{NO}_3 \times 35.0 / \text{salinity}$$

For $T < 4°C$
$$= 23 \mu \text{mol/kg}$$

For $4°C < T < 16°C$
$$= 30.7 - 1.92 \times T \mu \text{mol/kg}$$

For $T > 16°C$
$$= 0 \mu \text{mol/kg}$$

The calculated pCO$_2$ in open ocean surface waters ranged from 256 to 365 μ atm. The October values seem

![Graph](image-url)
to fall within 326 ± 7 µ atm north of the Polar Front. The values are distinguishably lower (311 ± 7 µ atm) near the Polar Front but again higher (319 ± 8 µ atm) south of the front. The November values seem to decrease steadily with increasing temperature (from 320 µ atm near ice edge) at the rate of 1.5% per °C. The values under the ice ranged from 332 to 365 µ atm, with an average of 354 ± 9 (1σ) µ atm (Chen, 1984, 1988). Theoretically, pCO₂ should increase with increasing temperature (Copin-Montegut, 1988). Our data indicate biological consumption.

Takahashi and Chipman (1982) also measured pCO₂ during the WEOLEX expedition. They reported pCO₂ between 307 and 340 µ atm in the open ocean surface waters. The surface values under ice ranged between 313 and 340 µ atm with an average of 325 ± 7 µ atm. The CO₂ partial pressure in the atmosphere was 341.3 ± 1.4 (1σ) µ atm on the average, slightly greater than the seawater values in the open ocean but similar to values in the ice field. The open water values obtained during the WEOLEX expedition in the austral winter of 1981 are generally similar to those of previous expeditions, such as the GEOSecs (Geochemical Ocean Section Studies) Atlantic Expedition in January, 1973, the GEOSecs Pacific Expedition in February — March, 1974, and the GEOSecs Indian Ocean Expedition in February, 1978. These observations indicate that the surface waters of the Antarctic Ocean are not a strong sink for atmospheric CO₂, in spite of their low temperatures; and are only slightly undersaturated during the late austral winter and most likely throughout the year. Waters beneath ice can not exchange freely with the atmosphere.

V. pH in the Subsurface Waters

The vertical pH distributions (Fig. 6) generally show a pronounced minimum near the broad maximum temperature (Tₘₐₓ) and salinity layer (Sₘₐₓ) (Fig. 7). The Sₘₐₓ layer is usually only 150 m below the Tₘₐₓ. A large portion of the Tₘₐₓ and Sₘₐₓ water at a typical station such as Stn 34 comes from modified Circumpolar Deep Water (CDW). By the time the CDW signal is incorporated into the Weddell Gyre from the Circumpolar Ocean and becomes Weddell Deep Water (WDW), it is characterized by high Apparent Oxygen Utilization (AOU) but low pH values. In deeper layers, the waters are modified by the Antarctic Bottom Water (AABW), and temperature, salinity and AOU decrease with depth, whereas pH values increase monotonically (Chen, 1982c; Gordon et al., 1984; Chen, 1984).

In a few cases, such as at Stn 36/37, the core of the warm water layer (250-1000 m) is warmer and saltier than that observed at Stn 34 and represents fresh CDW input from just north of the Weddell Gyre. The AOU values, whose calculation was based on the oxygen solubility given in Chen (1981), are lower, and a broad maximum in pH is found below the near-surface minimum (Fig. 7). This situation suggests that not as much decomposition of organic material has occurred in the circumpolar Sₘₐₓ water at Stn 36/37 than has occurred within the Weddell Gyre, represented by Stn 34. A second pH minimum is found at a much greater-depth (1200 m) at Stn 36/37, and pH again increases monotonically toward the bottom.

A composite θ/pH plot for all WEOLEX station samples is shown in Fig. 8. Waters within the Weddell Gyre all fall on approximately the same line of θ/pH correlation line, and the ones above this line all have large fresh input from CDW. The linearity of the θ/pH relation, a mirror image of what was found for θ/AOU correlation, suggests little in situ organic carbon production or decomposition (Poisson and Chen, 1987; Chen, 1988). There is a change in slope at about 0.1°C and σ₄ of 46.06, similar to what was observed on the θ/oxygen plot (Poisson et al., 1984). A σ₄ of 46.06 may roughly correspond with a stability maximum reported by Reid et al. (1977) and Reid (1989) and is close to the upper boundary for AABW as defined by Schlemmer (1978). The waters less dense than about 46.06 and 46.07 in σ₄ have entered from the Drake Passage and the waters...
possesses a slightly steeper slope, suggesting some contribution from deep waters richer in CDW. Another small break seems to be present at approximately -0.6°C and \( \sigma_4 \) of 46.16 with a steeper slope below. Waters denser than a \( \sigma_4 \) of 46.16 call for an even larger input from the CDW and yet start to show an excess CO₂ signal (Chen and Rodman, 1990). Gordon and Huber (1984) reported that the warm cells of CDW are eroded quickly in a single winter season. The excess heat brought up by CDW is lost to the atmosphere through the ice, but the excess salt is not necessarily compensated for by increased fresh water introduction. As a result, the pycnocline is destabilized most with a greater than normal injection of warm CDW, hence increasing the chance of deep convection. In the mean time, the water mixes with some surface water and picks up excess CO₂. This may explain why the bottom water contains a large portion of warm CDW and some excess CO₂.

It has been difficult to identify water masses in the Southern Ocean, because waters are relatively homogeneous, without clearly identifiable structures. The breaks in the \( \theta \)/pH correlations may be useful in defining water mass boundaries (Chen and Rodman, 1985).

It should be noted that all pH values within the linear range fall within an envelope approximately 0.014 pH units wide (Fig. 8). This spread includes both calibration and sampling errors, so the real station-to-station difference is probably small. In addition, these data clearly demonstrate that, contrary to some reports, pH can be measured rather precisely. Byrne et al. (1988) also demonstrated that pH can be measured accurately.

VI. Titration Alkalinity and Calcium in the Subsurface Waters

Both TA and calcium seem to behave conservatively, as expected (Weiss et al., 1979), because polar marine organisms are mainly siliceous, and little production or dissolution of CaCO₃ occurs in the Weddell Sea. The normalized TA (NTA) and calcium (NCa = Ca x 35.0/salinity) concentrations remain essentially constant (except for a very weak maximum in NTA near 0°C) and show little variation with depth or temperature (Poisson and Chen, 1987). The spread of the composite NTA values (average value 2386 µ eq/kg) is approximately 10 µ eq/kg, which includes sampling and measurement errors. The station-to-station difference, therefore, is probably also small.

Calcium measurements were made for only five stations (9, 27, 28, 36 and 37) with stored samples, some of which were frozen, unexpectedly, during transit. Calcium carbonate precipitates could have formed when the water froze, and some particles might not have redis-
solved when the ice melted. Also, some seawater might have been pushed out of the bottles when ice formed, again changing the overall composition of the sample. The composite NCa results, with an average value of 10240 μ mol/kg, have a large scatter (± 15 μ mol/kg vs. the precision with unfrozen samples, ± 5 μ mol/kg). Consequently, whether our calcium measurements represent real values is questionable. It is obvious, however, that no deep water maximum in NTA and NCa is found in the Weddell Sea, as is commonly found in the low and mid-latitudes (Chen, 1982c; Chen et al., 1982). Because the NTA and NCa values remain constant throughout the water column, they cannot be used as a water tracer in the Weddell Sea (Chen, 1984; Poisson and Chen, 1987).

VII. TCO₂ and pCO₂ in the Subsurface Waters

The TCO₂ of the Weddell seawater also seems to mix conservatively below the Sₘₐₓ layer (Poisson and Chen, 1987; Chen, 1988). The normalized TCO₂ values calculated from pH and TA data for all WEPOLEX stations below the Sₘₐₓ layer are plotted vs. θ in Fig. 9. A linear correlation is observed with a standard deviation of 6 μ mol/kg. Since the standard deviation of the least-squares fit is only slightly larger than our analytical precision of ± 5 μ mol/kg, station-to-station variation is minimal. A slight change in slope occurs at -0.6°C.

A linear regression of the normalized total CO₂ values of three GEOSECS (January, 1973) stations in the vicinity yields a standard deviation of 15 μ mol/kg. The best fit of the GEOSECS data (Takahashi et al., 1980) yields 2286.0 μ mol/kg at 0.2°C and 16.4 μ mol/kg lower at -0.8°C. The best fit of the WEPOLEX data yields 2281.5 at 0.2°C but only 14.4 μ mol/kg lower at -0.8°C. The difference between these two sets of data is smaller than the uncertainty in the analytical procedures and, therefore, does not necessarily indicate temporal variations occurring between 1973 and 1981. More and more excess CO₂ is expected to penetrate into the AABW before it is found in the warmer water originating largely from the old CDW. It would be interesting to observe in the future whether the NTCO₂ value at -0.8°C showed an increase relative to the 0.2°C water.

The θ/calculated pCO₂ correlation (Fig. 10) is a mirror image of the θ/pH correlation. There is a maximum near the Sₘₐₓ layer. Below it, the pCO₂ decreases roughly linearly with decreasing temperature, but a steeper slope is observed below -0.8°C. The measured pCO₂ values (Fig. 11; Takahashi, 1982) scatter badly because of operational difficulty during WEPOLEX. Nevertheless, the values agree reasonably with the calculated values.

![Fig. 9. θ/NTCO₂ correlation for all WEPOLEX samples below the maximum salinity layer. The arrow indicates a slight change in slope.](image)

![Fig. 10. θ/pCO₂ correlation for all WEPOLEX samples. Crosses and open circles denote, respectively, samples above and below the maximum salinity layer. The arrow indicates a slight change in slope.](image)

VIII. Carbon-13 in the Subsurface Waters
C.T. A. Chen

Fig. 11. T/pCO₂ correlations below the maximum salinity layer based on Takahashi's (1982) pCO₂ measurements during WEPOLEX.

The carbon-13 values (Kroopnick, 1985) again indicate conservative mixing in the Weddell Sea. For instance, two linear segments representing data above and below the Smax layer, respectively, are observed on the S/δ¹³C plot (Fig. 12). This plot is similar to the S/NO plot (Broecker, 1974; Fig. 13).

Fig. 12. Salinity vs δ¹³C at GEOSECS Stn 89.

Fig. 13. Potential temperature and salinity vs. NO at WEPOLEX Stn 36/37.

The θ/δ¹³C correlation is shown in Fig. 14. This plot does not look like the θ/NO plot (Fig. 13) but is a mirror image of the θ/NTCO₂ plot (Poisson and Chen, 1987). The water with the minimum potential temperature is the remnant winter water (Chen, 1988). Assuming that this remnant winter water is a mixture of the surface water left over from summer and the upwelled WDW, this author obtained a surface/WDW mixing ratio of 63/37 based on the δ¹³C data. This ratio agrees well with the value 68/32 based on nitrate data (Chen, 1984; Poisson and Chen, 1987), 75/25 based on oxygen data (Gordon et al., 1984) and 69/31 based on ³He data (Schlosser et al., 1987).

XI. Conclusion
Weddell Sea Descriptive Chemical Oceanography

The values of pH in surface waters of the southern South Atlantic Ocean and the Weddell Sea decrease with decreasing temperature, but NTA, NTCO₂, NNO₃, NPO₄, and NSIO₃ increase with decreasing temperature. The surface pCO₂ values remain constant in October but increase with decreasing temperature in November.

The pH and δ¹³C correlate linearly with δ for subsurface waters with higher pH and δ¹³C values at lower temperatures. NTCO₂ and pCO₂ also correlate linearly with δ for subsurface waters but with higher values at higher temperatures. NTA and NCa do not correlate with temperature for subsurface waters. The δ¹³C data suggest a surface/WDW mixing ratio of 63/37.

Acknowledgements

Data analysis and writing were supported by the National Science Council (NSC 80-0209-M110-08). An anonymous reviewer provided valuable comments. Ms. Chiu-Ping Candy Lin typed the manuscript.

References

C.T. A. Chen

and A. Gordon (1983) Reports of the US-USSR Weddell
Polynya Expedition: Vol. II-hydrographical data LDGO 83-1,
pp. 115.

Kroopnick, P.M. (1985) The distribution of 13C of CO2 in the
World Oceans. Deep-Sea Research, 32, 57-84.

Marra, J. and D. Boardman (1984) Late winter chlorophyll a
distribution in the Weddell Sea. Mar. Ecol. Prog. Seis, 19, 197-
205.

Marra, J., L.H. Burckle and H.W. Ducklow (1982) Sea ice and
water column plankton distributions in the Weddell Sea in

Olson, E.J. and C.T. Chen (1981) Interference in the determina-
tion of calcium in seawater. Limnology and Oceanography,
27, 375-380.

Poisson, A. and C.T.A. Chen (1987) Why is there little anthropo-
genic CO2 in the Antarctic Bottom Water? Deep-Sea Re-
search, 34, 1255-1275.

Reid, J.L. (1969) On the total geostrophic circulation of the
South Atlantic Ocean; flow patterns, tracers, and transports.
Progress in Oceanography, 23, 149-244.

Reid, J.L., W.D. Nowlin, Jr. and W.C. Patzert (1977) On the
characteristics and circulation of the southwestern Atlantic

Schlemmer, F.C. (1978) Structure and spreading of Antarctic
Bottom Waters in oceanic basins adjacent to Antarctica.
Ph.D. dissertation, Texas A&M University, pp. 127.

of the upper layers of the northwestern Weddell Sea. Deep-


Takahashi, T. and D. Chipman (1982) CO2 partial pressure in sur-
face waters of the Antarctic Ocean during the US-USSR
Weddell Polynya Expedition. Antarctic Journal, 1982 Review,
103-104.

Takahashi, T., W.S. Broecker, A.E. Bainbridge and R.F. Weiss
(1980) Carbonate chemistry of the Atlantic, Pacific, and
Indian Oceans: The results of the GEOSECS expeditions,
1972-1978. Lamont-Doherty Geological Observatory Tech-

Tsunogai, S., M. Nishimura and S. Nakaya (1968) Complexometric
titration of calcium in the presence of larger amounts of mag-

studies of the Weddell Sea. Deep-Sea Research, 26, 1093.

威得海之描述性海洋化学

陳 鎮 東

國立中山大學海洋地質研究所

摘要

1981年冬天作者參加了威得海冰中湖 (polynya) 探勘研究，工作人員利用蘇聯破冰船蘇莫號 (Somov) 首次取得了電
導、溫度、壓力 (CTD)、鹽度、氧氣、營養鹽、pH、鈣、總鹼度、總二氧碳酸及二氧化碳分壓之冬季資料。這些數據代
表了在全球海洋底層水形成區之形成時之原始濃度。利用所取得冬季資料與文獻中已有之夏季資料相比得：極區鋸縫
(Polar Front)南側之化學性質差異頗大；威得海表水之二氧化碳分壓僅較海中之分壓稍低；凈圖之混合主導化學性
質。如pH、氧氣、總二氧化碳及二氧化碳分壓之分佈，而上述數據有助於研究威得海中水團之來源；鈣及總鹼度資料無
法用於分辨水團；深水並未完全混合均勻，而顯現若干不連貫面；湧昇至表層之威得海深層水占表層水成份之三分之一。