Use of pH to trace water masses in the Weddell Sea

Chen-Tung Arthur Chen

Abstract: When plotting the pH data obtained in the eastern Weddell Sea vs. potential temperature (θ), a distinct break occurs in the slope near θ = 0.08°C and σ = 46.06. A less pronounced break occurs at θ = -0.6°C and σ = 46.16. Total CO₂, pCO₂ and silicate data also show similar discontinuities. The breaks in the pH slopes probably result from, and can be used to help identifying the lateral spreading of deep- and bottom-water masses.

1. Introduction

Deep waters from the three oceans move to the Southern Ocean. The resultant relatively homogeneous water (Montgomery, 1968; Carmack, 1977) becomes the major source of the Antarctic Bottom Water (AABW), which spreads back into the deep world oceans (Wüst, 1959; Lynn and Reid, 1968). The Weddell Sea is considered the major source of the AABW (Deacon, 1937; Reid and Lynn, 1971; Carmack and Foster, 1975; Carmack, 1990).

Relative homogeneity of the water masses, however, results in small signals for traditional tracers such as θ, S, and oxygen. As a result, it is more difficult to clearly identify the end members of the water masses. On the other hand, it is not unexpected that the deep Weddell Sea waters possess distinct regimes despite of the relative homogeneity (Callahan, 1972; Reid et al., 1977; Schlemmer, 1978; Foster and Middleton, 1979; Gordon, 1978, 1982; Chen and Rodman, 1985, 1990; Orsi et al., 1993). In this report I will use pH, total CO₂, pCO₂ and silicate data in addition to the traditional tools to identify in more detail the water-mass characteristics of the important end-members. These end members constitute the water masses in the Weddell Sea either directly or indirectly. Data were mainly collected on the Soviet icebreaker SOMOV during the US-USSR Weddell Polynya Expedition in the late austral winter and early spring of 1981 (Huber et al., 1983; Chen, 1984). Additional GESECS, AJAX and Polarstern data (GESECS, 1981; Chipman et al., 1986; Chipman and Takahashi, 1990) are also used.

2. pH, total CO₂, pCO₂, and silicate signals

The study area and the cruise track are shown in Fig. 1. The pH samples were all determined at 25 ± 0.02°C with a combination electrode within 30 minutes. NBS 4.004 and 7.415 buffers were used to calibrate the electrode. In addition, a NBS 6.863 buffer plus three buffers 4.01, 6.86 and 9.18 prepared by V. Fedorov (the Arctic and Antarctic Research Institute of the USSR) were measured. The results agreed with the prepared values to 0.005 ± 0.005. The reproducibility of the pH measurements was better than ±0.003 units for 4 replicates of each sample. The electrode drift was determined approximately every two weeks. The largest drift was found to be 0.001 unit/day and the correction was made to the measured values (Chen, 1984).

Alkalinity was determined at 25 ± 0.02°C with a Radiometer TTT61 Digital Titrator with a reproducibility of better than ±4 μmol/kg for replicate samples. Some samples were also measured using the method of Culherson et al. (1970) with similar precision. No systematic 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. Total CO₂ (TCO₂) and pCO₂ were calculated from pH and alkalinity with a precision of 5 μmol/kg and 5 μatm, respectively. In Fig. 2 is plotted potential temperature (θ) vs. pH for the deep SOMOV data (Chen, 1984).
Fig. 1. Location of the SOMOV vertical stations. Dotted lines at 20 Oct. and 14 Nov. 1981 locate the ice edge.

Fig. 2. Composite SOMOV potential temperature vs. pH diagram for data below the salinity maximum; x's are data above salinity maximum. Characteristics of a, b and c are listed in Table 1 and discussed in the text.
Fig. 3. Composite SOMOV sigma-4 vs. pH diagram. Characteristics of a, b and c are listed in Table 1 and discussed in the text.

Fig. 4. Composite SOMOV silicate vs. pH diagram. Characteristics of a, b and c are listed in Table 1 and discussed in the text.
Table 1. Characteristics at the Deep-Water Discontinuities in the Weddell Sea

<table>
<thead>
<tr>
<th></th>
<th>TOP—(a)(^{(1)})</th>
<th>BREAK 1—(b)(^{(2)})</th>
<th>BREAK 2—(c)(^{(2)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (^{\circ}\text{C})(^{(0)})</td>
<td>0.19—0.2(^{\circ}\text{C})</td>
<td>0.05 to 0.08</td>
<td>-0.5 to -0.6</td>
</tr>
<tr>
<td>pH</td>
<td>7.73</td>
<td>7.750 to 7.757</td>
<td>7.779 to 7.789</td>
</tr>
<tr>
<td>TCO(_3) ((\mu\text{mol/kg}))</td>
<td>2282</td>
<td>2280</td>
<td>2268</td>
</tr>
<tr>
<td>pCO(_2) ((\mu\text{atm}))</td>
<td>520</td>
<td>510</td>
<td>460</td>
</tr>
<tr>
<td>S</td>
<td>34.680</td>
<td>34.683</td>
<td>34.660</td>
</tr>
<tr>
<td>Si ((\mu\text{mol/kg}))</td>
<td>124.5</td>
<td>129.5</td>
<td>125.5</td>
</tr>
<tr>
<td>AOU ((\mu\text{mol/kg}))</td>
<td>148</td>
<td>135</td>
<td>111</td>
</tr>
<tr>
<td>(\sigma_t)</td>
<td>27.838</td>
<td>27.843</td>
<td>27.861</td>
</tr>
<tr>
<td>(\sigma_t)</td>
<td>37.123</td>
<td>37.158</td>
<td>37.219</td>
</tr>
<tr>
<td>Av. depth (m)</td>
<td>312 (\pm) 151</td>
<td>1241 (\pm) 131</td>
<td>3944 (\pm) 156</td>
</tr>
</tbody>
</table>

\(^{(1)}\) TOP refers to the top of the deep water, see Fig. 2, for locations of a, b, c

\(^{(2)}\) The ranges recorded are due to slightly different values given when different parameters are plotted.

There is a distinct break in slope near \(\theta = 0.08 \, ^{\circ}\text{C}\) and a less pronounced break near \(\theta = -0.5 \sim -0.6 \, ^{\circ}\text{C}\). When \(\sigma_t\) (Fig. 3; density reference to 4000db surface, Reid and Lynn, 1971) is plotted against pH, changes in the pH slope are seen at \(\sigma_t = 46.06\) and 46.16. The \(\sigma_t = 46.06\) layer separates the circumpolar water and the Weddell Sea Deep Water (WSDW) whereas the \(\sigma_t = 46.016\) layer separates WSDW from the Weddell Sea Bottom Water (WSBW, Orsi et al., 1993).

The deeper discontinuity, at \(\sigma_t = 46.16\), is more distinctly shown in the silicate/pH diagram (Fig. 4), than on the other figures. Table 1 gives the characteristics of the two discontinuities determined from the complete SOMOV data set. The depth, the \(\sigma_t\) (density reference to 2000db surface) and the \(\sigma_t\) surface associated with the appropriate \(\sigma_t\) surface are average values computed from the total SOMOV data.

AOU is the apparent oxygen utilization which is the difference between the measured oxygen concentrations and the saturated values calculated using Chen (1981).

TCO\(_3\) of the Weddell seawater seems to mix conservatively below the \(S_m\) layer. The normalized TCO\(_3\) (NTCO\(_3\) = TCO\(_3\)×35/S) values calculated from pH and alkalinity data for all SOMOV stations below the \(S_m\) layer are plotted vs. \(\theta\) in Fig. 5. A linear correlation is observed with a standard deviation of 6 \(\mu\text{mol/kg}\), since the standard deviation of the least-squares fit is only slightly larger than our analytical precision of \(\pm 5 \, \mu\text{mol/kg}\), station-to-station variation is minimal. The change in slope at approximately \(-0.6 \, ^{\circ}\text{C}\) is not apparent. No break in slope near 0.1\(^{\circ}\text{C}\) is observed.

Fig. 5. \(\theta / \text{NTCO}_3\) correlation below the maximum salinity layer. Characteristics of a, b, and c are listed in the Table 1 and discussed in the text.
investigated the distribution of properties on six $\sigma_t$ surfaces which marked the boundaries of various abyssal water masses and/or were characterized by changes in gradients. Gordon (1982) has made a detailed study of WSDW variability, Foster and Middleton (1979) and Orsi et al., (1993) analyzed the variability within the bottom water of the Weddell Sea. We believe that the pH slope breaks result from similar lateral spreading of deep and bottom water masses.

In Table 2 the water-mass characteristics have been presented for the important end-members which should affect this region either directly or indirectly. It should be noted that the values given for the Circumpolar Deep Water (CDW) components represent a concentrated mass in the Southwestern Atlantic. Also the WSDW may have a relatively large non-steady state temperature and salinity range (Gordon, 1982).

Significant dilution of these deep water end-members has occurred in transit to the basins near Antarctica, probably with a complex mixing history (Callahan, 1972). The CDW entering the Southwestern Atlantic has low oxygen and high nutrients which originate from the Pacific Deep Water, PDW. It encounters in the same density range the higher oxygen, lower nutrient and markedly higher salinity North Atlantic Deep Water (NADW) (Reid et al., 1977). The incorporation of the NADW into the CDW results in a low-oxygen component above a broader high-salinity component which becomes decreasingly separated vertically upon approaching the Antarctic Continent (see for example plates 110, 111, 113 in Gordon et al., 1982). The CDW undergoes further modification in the Weddell Sea by the input of Antarctic components, becoming considerably colder, fresher, more oxygenated, and starting to show traces of anthropogenic components such as tritium, carbon 14, freons, and fossil fuel CO$_2$ (Weiss et al., 1979; Chen, 1982; Poisson and Chen, 1987; Chen and Rodman, 1990; Anderson et al., 1991). The CDW is now essentially a new deep water mass frequently referred to as WSDW (Gordon, 1978; Gordon and Uber, 1984); however, the low oxygen signal overlying a high salinity signal is still
Table 2. Water Mass Characteristics in the Drake Passage, South Atlantic and Weddell Sea

<table>
<thead>
<tr>
<th>Water Mass</th>
<th>$\theta$ (°C)</th>
<th>S</th>
<th>$O_2$ (ml/l)</th>
<th>$SiO_2$ (µmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter Surface Water (WW)</td>
<td>$t_r$ to $-1.5^\circ$</td>
<td>33.8 to 34.6</td>
<td>6.9 to 7.5</td>
<td>70$^{34}$</td>
</tr>
<tr>
<td>Summer Surface Water (SW)</td>
<td>$&gt;t_r$</td>
<td>$&lt;34.2^\circ$</td>
<td>$&gt;7.8^\circ$</td>
<td>70$^{32}$</td>
</tr>
<tr>
<td>Shelf Water</td>
<td>$t_r$ to $-1.5^\circ$</td>
<td>34.2 to 34.8</td>
<td>7.1</td>
<td>70$^{36}$</td>
</tr>
<tr>
<td>Modified Warm Deep Water$^{(a)}$</td>
<td>-1.6 to 2$^\circ$</td>
<td>34.35 to 34.7</td>
<td>5.5 to 7.2</td>
<td>65 to 85$^{36}$</td>
</tr>
<tr>
<td>Weddell Sea Deep Water (WSDW)$^{(b)}$</td>
<td>0 to 2$^\circ$</td>
<td>34.65 to 34.75</td>
<td>4.3 to 5.3</td>
<td>90 to 120$^{36}$</td>
</tr>
<tr>
<td>Pacific Deep Water (PDW)</td>
<td>1.8 to 2.5$^{(55)}$</td>
<td>34.55 to 34.7</td>
<td>3.7 to 4.6</td>
<td>60 to 100$^{35}$</td>
</tr>
<tr>
<td>North Atlantic Deep Water (NADW)</td>
<td>2 to 3$^{(56)}$</td>
<td>34.8 to 34.95</td>
<td>4.5 to 5.5</td>
<td>50 to 70$^{36}$</td>
</tr>
<tr>
<td>Weddell Sea Bottom Water (WSBW)</td>
<td>$&lt;-7^\circ$</td>
<td>34.65</td>
<td>6.5</td>
<td>95 to 115$^{35}$</td>
</tr>
<tr>
<td>Antarctic Bottom Water (AABW)</td>
<td>-0.4$^\circ$ to 0$^\circ$</td>
<td>34.6 to 34.68</td>
<td>5.4 to 5.8</td>
<td>110 to 123$^{36}$</td>
</tr>
</tbody>
</table>

(1) CARMACK, (1977); the $t_r$ refers to freezing temperature
(2) CARMACK, (1974)
(3) WEISS et al. (1979)
(a) These values have been taken from the temperature-minimum water
(b) Summer values
(4) GEOSecs Atlantic Expedition Vol. 2 (1981); plates 3, 5, 11, 15 are the Western Atlantic
and into the Scotia Sea; plates 55 and 59 are for the Drake Passage; oxygen values are
given in µM/kg and have been converted to ml/l.
(5) GORDON et al. (1982)
(c) plates 184, 185, 186 are a detailed transect across the Drake Passage.
(d) plate 104 is for the South Atlantic
(6) Weddell Sea Deep Water is also sometimes referred to as warm deep water.
(7) Fuster and Middleton (1979)
(8) CARMACK (1973)
(9) The upper boundary of AABW has been somewhat arbitrarily chosen to be 0° to fit with
the lower boundary of WSDW.

Identifiable. Within the shelf domain the WSDW is further modified.
End-members were estimated from Table 2 and from Figs. 2–6. Because precise pH measurements are non-existent for most of these water masses, assigning end-member points in these figures is somewhat tentative. In looking for the end-member (Fig. 2) for the regime denser than $\sigma_t = 46.156$ (Fig. 3), we note that a shelf component at freezing temperature would have a pH of about 7.80 to 7.81. This translates from extrapolation on Figure 8 into a salinity range of 34.65 to 34.66, easily within the shelf-water range in view of the large salinity spread it may have (Table 2). However, shelf-water components in bottom-water formation must be of these higher salinity varieties.

For the warmer end-member, the WSDW end of this mixing line defined at a temperature of 0.8–1.2°C, we see a pH of about 7.76 and, thus,
again by extrapolation on Figure 8, a salinity of 34.66 to 34.67. These salinities correspond to the range of WSDW (Table 2). When this mixing line is extended to 2.5 to 3°C the corresponding pH of 7.73–7.74 gives a salinity of at most 34.69, much below that for NADW. However, from the combined SOMOV θ/S data (Fig. 8, Gordon and Huber, 1984) we can see that the abyssal regime has a non-isopycnal scatter which would also give significantly lower salinities than NADW from a simple two-component mixing line, indicating a complex mixing history for the predominantly isopycnally spreading deep waters. Extension of the mixing line for the second regime (σ = 46.056 to 46.156) to the warmer end-member WSDW component at 0.8–1°C gives a pH of 7.71–7.72 and a corresponding extrapolated salinity of 34.70 to 34.71. Further extension of the line to 2.5–3°C gives a pH of 7.60–7.64 and a salinity extrapolated to 34.79 to 34.83, consistent with values for NADW (Table 2). The cold end-member for this mixture can be explained as Winter Water (WW) at freezing, with a pH of 7.85 and thus an extrapolated salinity of 34.60.

The upper regime between a σ of 45.900 and 46.056 can be explained as a mixture of WW (t = freezing temperature, pH = 7.92–7.94, S = 34.67 to 34.68) and the oxygen-poor component of WSDW. For example, at t = 0.6 to 0.8°C the pH is 7.69 to 7.71 which then gives a salinity of 34.68 to 34.69. Extending this mixing
line to even warmer values of $2-2.5^\circ$C of PDW will give extrapolated salinities in the range 34.68 to 34.70 from a pH range of 7.54 to 7.59.

Vertical convection of WW with entrainment of WSDW at progressively more southern locations, or deeper convection by increasingly dense WW, or a combination of these two effects, and subsequent spreading of the mixture after reaching their equilibrium density, may explain these separate deep water regimes. The bottom-water regime is similarly explained, but instead of winter water entering directly into the mixing processes, shelf water is entraining modified deep water. Observed variability in the WSBW, (Table 2), a subclass of AABW on a year's time scale, may in part be related to seasonal effects (Foster and Middleton, 1979). It is significant to this study that Carmack and Foster (1975) note a $\theta/S$ discontinuity near $-0.5^\circ$C and $\sigma_z = 46.175$ which they attribute to either older re-circulated WSBW or an additional AABW component. Krysell (1992) plotted carbon tetrachloride and methyl chloroform concentrations vs $\theta$ and also found a distinct break at $-0.5^\circ$C. The man-made chemicals could only be detected in the cold bottom waters with $\theta < -0.5^\circ$C. This water is the most ventilated of all subsurface waters with the highest oxygen, tritium and C-14 (Table 2; Chen and Rodman, 1990). Chen and Rodman (1990) also reported that bottom waters denser than $\sigma_z = 46.156$ contain some anthropogenic CO2.

Shelf-water modified deep water mixtures and subsequent spreading at depths have been analyzed off Wilkes Land by Carmack and Kilworth (1978) and observed off Enderby Land (Jacobs and Georgi, 1977). In both cases they observed plumes formed. But the data here suggest a broader spatial effect, since the three
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![Graph showing oxygen and potential temperature vs. salinity](image)

Fig. 9. SOMOV station 30 oxygen and potential temperature vs. salinity taken from the oxygen probe and CTD. The $\sigma_z$ surfaces which encompass the two breaks (Table 1) are shown (taken from HUBER et al., 1983).

Regimes extend over several kilometers depth and well north of the Antarctic continent. The cyclonic circulation (KLEPIKOV, 1960; DEACON, 1976, 1979; CARMACK and FOSTER, 1975) in the Weddell Sea may enhance and spread the effect of plume injection by providing a longer path for alterations to occur. Major injection of surface water directly into the deep-water regime via deep convection has been observed in this region (GORDON, 1978), and modeling studies (KILWORTH, 1979; MARTINSON et al., 1981) have shown that large areas of the Weddell Sea may be subject to this deep convection, called chimneys. GORDON (1982) hypothesizes that chimney convection results in the significant temporal and spatial thermal alterations (the $\theta$ vs $\sigma$ is lowered by as much as 0.4°C) observed between 250 m and 2700 m over broad areas. It is interesting to note that anomalously oxygenated fresh water is observed well north of the Antarctic continent in the deep water between $\sigma_s$ of 46.056 and 46.156. (Fig. 9).

Figure 10 shows a potential density section of pH data for the eastern stations of the SOMOV track. The mixed layer is at densities less than a $\sigma_z$ of about 27.65, and the pycnocline extends to a $\sigma_z$ of about 27.80. Few data points exist in the pycnocline so the contour interval is necessarily coarser and more subjective. Below $\sigma_z=27.8$ the isopleths of pH become increasingly level showing that the distribution of pH is dominated by isopycnal spreading. Some structure is seen in the 7.750 and 7.740 pH contours where they bow slightly upward at stations 7 and 9 indicating some non-isopycnal spreading. The density surfaces less than a $\sigma_z$ of 27.82 curve slightly downward at these stations (see Fig. 2 in GORDON and HUBER, 1984), and thus the pH contours lying more horizontally with respect to density contours (shown by GORDON and HUBER, 1984) would account for the observed bowing of the pH isopleths. The minimum pH lies from a $\sigma_z$ of 27.82 to 27.84 which is the density range containing the oxygen minimum. Thus the spread of pH in the deep and bottom waters is very much isopycnal.

4. Conclusion

pH is easy to measure, has high precision and accuracy, and the analysis for 12 Rosette samples (4 replicates for each sample) can be done within 30 minutes (CHEN, 1984; BYRNE et al., 1988). It proves to be very useful in studying water masses in the Weddell Sea. Distinctive breaks in the pH vs $\theta$ plots at $\theta=0.08^\circ$ C and $-0.6^\circ$ C were related to spreading of deep- and
bottom-water masses in the Weddell Sea.

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References


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ウエッデル海におけるpHの利用による水塊の追跡

Chen-Tung Arthur Chen

要旨：東部ウエッデル海で得られたpHのデータを温層（θ）に対してプロットしたところ、θ = 0.08℃、σ = 46.06近辺で顕著な傾斜の断絶が認められた。またθ = -0.6℃、σ = 46.156近辺でもこれよりやや不明瞭な断絶が生じた。全CO2、pCO2、およびケイ酸のデータも同様な不連続性が見られた。このpH傾斜に見られる断絶は、おそらく深層および底層水塊に起因しているものと考えられ、両水塊の挙動動への拡がりを識別する手助けとして利用できるものと考えられる。