THE DISTRIBUTION OF COPPER, ZINC AND CADMIUM IN THE SOUTHERN OCEAN SOUTH OF SOUTH AFRICA.

∇ ABSTRACT

Analysis and interpretation was carried out on trace metal samples (Cu,Zn,Cd) collected in the Southern Ocean south of South Africa. The results tentatively show that there is a significant copper flux from interstitial waters of the Weddell - Enderby basins. There is little evidence that these trace metals follow the systematics of nutrients throughout the water column; advection appears to play an important role in determining the vertical distribution of these chemical components.

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Introduction

Interpretation of the systematics of trace metal distribution in the oceanic environment has always been a difficult task due to their low levels and serious contamination at the sampling stage (Edmond,1980; Boyle et al.,1976). This problem was especially serious in the early days, as can be seen by comparing pre-GEOSECS (Schutz and Turekian,1965) and post-GEOSECS data (Boyle et al., 1976; Bender and Gagner,1976; Boyle and Edmond,1975). Most of the available data must be critically evaluated both in terms of sampling methods and absolute magnitudes.

The large amount of data gathered in the course of GEOSECS led to considerable improvement in the quality of the data as sources of contamination were identified and methods standardized. This was done through field exercises to compare sampling vessels (Bewers and Windom,1982) and inter-calibration tests (Bewers et al.,1981). As a result, the magnitudes of the trace metal concentrations are now at a lower level and show better agreement. It has further been found that the distribution of some trace metals such as cadmium (Boyle et al., 1976) and zinc (Bruland et al.,1978) follow the systematics of better quantified nutrients such as phosphate and silicate respectively. This type of correlation has led workers to extend this model to a global scale and use it as a test of the reliability of the data (Bruland et al.,1978; Danielsson,1980). In view of the data from this study and some of the literature data it is felt that this type of observed correlation may be a fortuitous result of highly productive waters as opposed to a global phenomenon. There are, especially in the Southern Ocean, a multiplicity of biogeochemical equilibria and physical processes that would distort an idealized distribution of a given parameter relative to another. Such processes as the flux of interstitial water from the siliceous sediments of the Weddell-Enderby basin are shown in this study, to distort the predicted Cu/Si ratio of Bottom Waters.

For the purposes of geochemical balance models it is in fact advantageous to have as many independent chemical variables as possible.

Thus, though the overall objective of the present study was to survey the trace metal distribution in the Southern Ocean, some of the more specific questions to be investigated were:

1. What are the baseline trace metal concentrations in these waters ?

2. Can water masses in the Southern Ocean be characterized by a particular trace metal content or ratio ?

3. How does the hypothesized silicate flux from the sediments affect the copper distribution in overlying waters ?

4. Can trace metals be used as mixing tracers in the vicinity of frontal mixing zones ?

In this project sampling was carried out for the major physicochemical parameters (T, S, O_2, Si, PO_4, NO_3) and seven trace metals (Mn, Ni, Co, Cu, Zn, Cd, Pb).

The stations were all worked from a ship of opportunity hence the locality of sampling was not ideal and this made interpretation difficult at times. The sampling region falls within the Atlantic-Indian sector (0° - 40°E) which has had its circulation dynamics well characterized through the data of recent cruises to the area (Jacobs and Georgi,1977). The dynamics and properties of the major water masses and zones have been extensively reviewed in the literature and are referred to below in the discussion of physical properties.

During the project,two cruises,"S.A. Agulhas" cruise 12 and 18 were carried out over a 2 year period (Fig.2.1).Unfortunately the trace metal data from cruise 12 could not be used due to unacceptably high values.

In the course of cruise 12 a line of 15 stations was worked from 64°S,4°E to Cape Town and it intercepted the Weddell drift. The second cruise(18) was part of the FIBEX* project and three legs of 4 stations each were worked. The two southerly legs (AG 1-8) were designed to straddle the Antarctic divergence zone and the third (AG 9-12) spanned the Antarctic Convergence region.

The discussion is divided into two main sections:

1 - Physical Oceanography
2 - Trace Metal Geochemistry

The Physical Oceanography is essentially a descriptive discussion concentrating mainly on two meridional legs worked in the course of "S.A. Agulhas" cruises 12 and 18. The Physical background assists in placing the geochemical aspects into the context of the circulation features of the region.

The Geochemistry section discusses aspects of the mechanisms and the factors affecting the distribution of the nutrients and trace metals.

The spatial scale of analysis is large; hence many of the points discussed are based on a number of assumptions that cannot immediately be tested. This arises from the survey nature of the project.The data appear in a separate appendix.

2. PHYSICAL OCEANOGRAPHY

The major transect discussed below, spans the Antarctic Convergence (AAC) from(54^{o} 33'S, 29^{o} 22'E)to Marion Is. (47^{o} 07'S, 37^{o} 11'E)(Fig.2.1). This line of stations AG 9-12 was worked in the course of the "S.A. Agulhas" cruise 18 when a further 2 legs of four stations each, straddling the Antarctic Divergence region were completed.

The latter lines were found to be of limited usefulness; hence their data will only be used in the context of the discussion on the trace metal distribution in the Southern Ocean. In the course of a previous cruise, "S.A. Agulhas"12, a meridional transect of 15 stations AG 49-63 with sampling to 2000m, was worked from(64^{o}S 4^{o}E) to Cape Town (Fig.2.1). This data will be discussed in the context of Antarctic Intermediate Water and Weddell Gyre sections.

2.1 Sub Antarctic Mode Water

Antarctic Intermediate Water

The mechanism associated with the formation of AAIW has been a source of dispute among workers since the existence of the salinity minimum layer was established by Deacon,(1937)(Deacon, 1982,Jacobs and Georgi,1977,Piola and Gordon,1982). The fact that the characteristics of the salinity minimum layer can be traced to a surface layer in the vicinity of the Antarctic Convergence (Deacon,1982), led to the conclusion that the mechanism was associated with the hydrodynamics of this frontal zone. Thus differences were based on the actual processes occuring at the front, which led to the formation of AAIW. Initial evidence led Sverdrup to propose that convergent flow at the frontal zone resulted from northward Ekman transport arising from the westerly wind stress (Deacon,1982) but serious deviations between the convergence zone and the zone of maximum wind stress led to the alternative concept of thermohaline circulation (Deacon 1937). A better understanding of frontal dynamics has led to recent ideas such as cross frontal mixing of Antarctic and Sub Antarctic waters as being more consistent with modern observations. (Jacobs and Georgi,1977). An alternative hypothesis that the salinity minimum results from the coldest and freshest (S < 34.20 $^0/oo$) layers of SAMW, formed by winter cooling in the southeast Pacific Ocean and advected to the Atlantic Ocean (McCartney,1977). Recently however, a detailed analysis by Piola and Gordon (1982) has shown that the evidence contradicts the SAMW idea in the Atlantic Ocean and that in reality both mechanisms may function but one predominates at any given region.

Characteristics and Distribution

At each of the meridional legs of the cruises, the Antarctic convergence zone was located as that zone lying imediately to the north of the temperature minimum ($t < 1^0C$) layer resulting from winter freezing of Antarctic zone surface water. In the course of cruise 18, an XBT section showed the convergence to lie near(50^0 30'S) at a longitude of 30^0E (Fig.2.2) The temperature section of cruise 12 showed a sharp thermal front separating the Weddell Gyre water from the warmer Circumpolar Deep Water (Fig.2.9a). This was

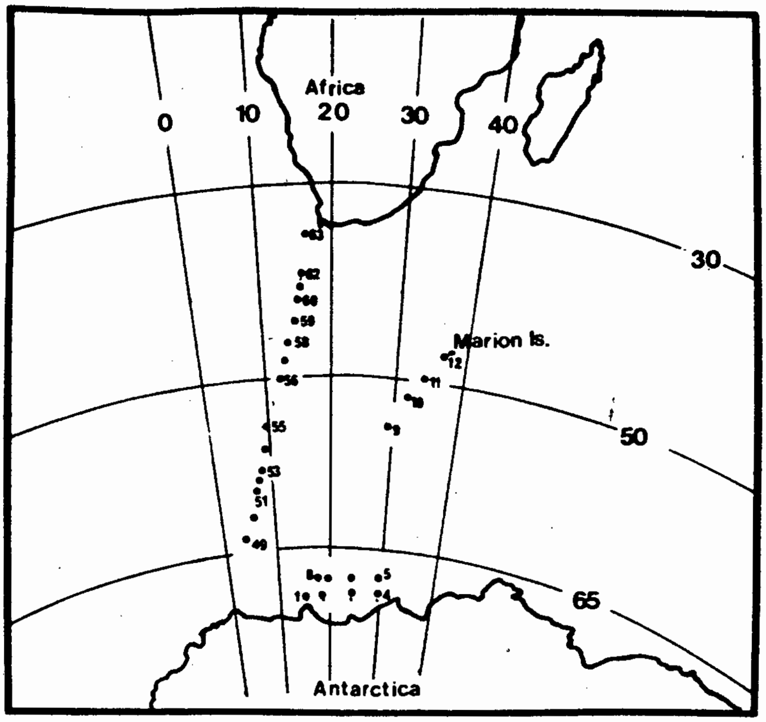


Fig. 2.1 Stations occupied in the course of "S.A. Agulhas" cruise 12 (49-63) and cruise 18 (1-12).

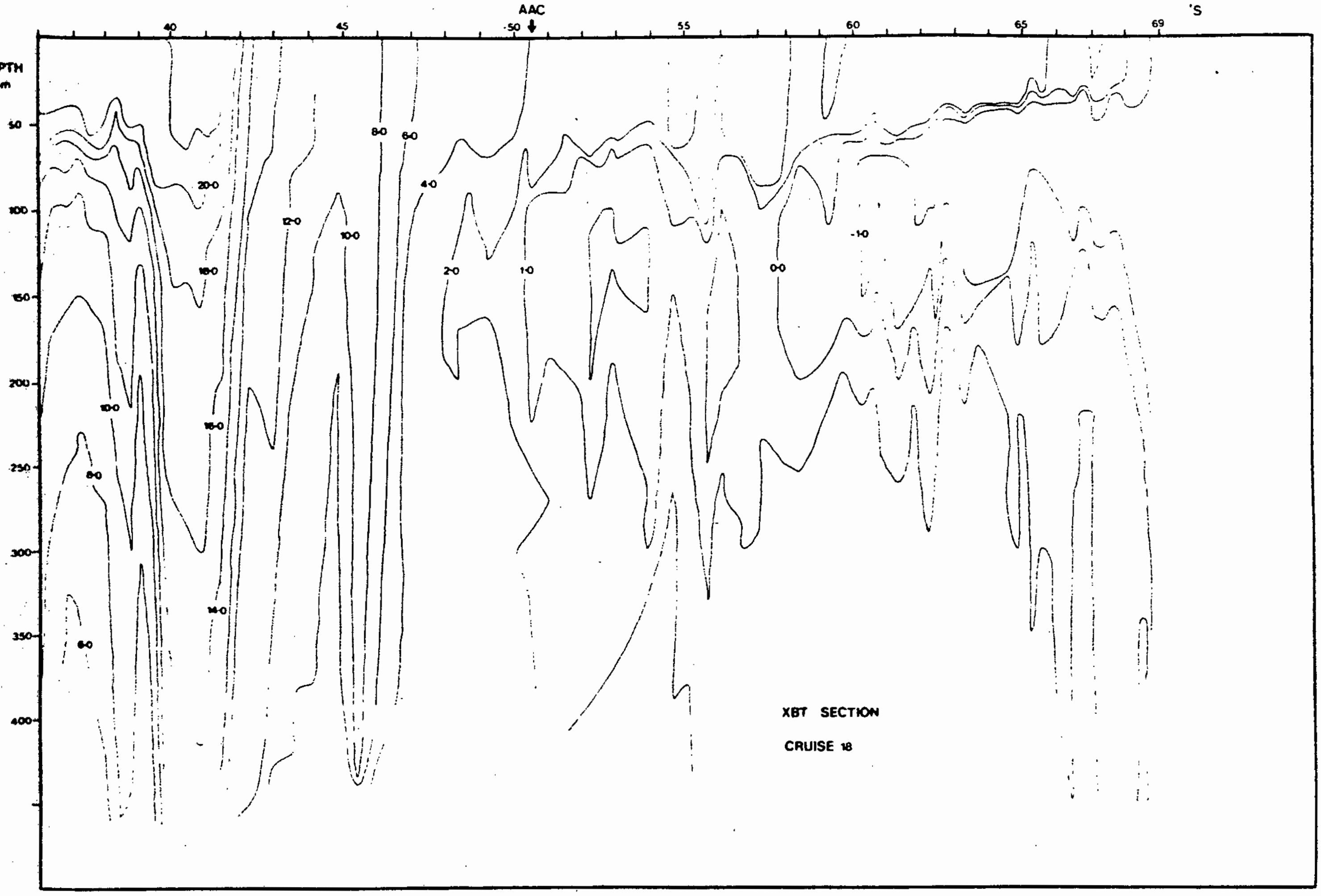


Fig. 2.2 An XBT section through the Southern Ocean at a nominal longitude of 30^{O}E.The position of the start of the Antarctic Convergence Zone is marked at a latitude of 50^{O}30'S (AAC)

located at 53^{0}S.

The characteristics of AAIW have been extensively investigated in this Atlantic Indian area (Jacobs and Georgi,1977) and comparisons made with similar features in the whole Southern Ocean (Piola and Gordon,1982). The main finding for this region is that the AAIW is divided into two distinct types; one saline(Indian Ocean) and the other fresher(Atlantic Ocean) (Piola and Gordon,1982)

The AAIW oxygen maximum and salinity minimum cores can be observed to develop from stations AG 59 to AG 62 near the South African continental slope.(Figs.2.3;2.4a-f) The salinity minimum is only observed to the north of the Sub-Tropical convergence,at AG 58 (46^{0}S),due to Sub Antarctic water being of low salinity ($S <$ $34.10^{0}/oo$). The salinity and temperature properties of the salinity minimum core of AAIW change from $34.17^{0}/oo$,3.22^{0}C at AG 58 to $34.40^{0}/oo$,5.26^{0}C at AG 63 (Fig.2.4a-f) The CTD traces (Fig.2.4a-f) show extensive structure in the vicinity of the salinity minimum layer. The salinity traces show an erosion of the low salinity southerly water by high salinity intrusions along isopycnal surfaces.

These high salinity excursions can be ascribed to the warmer,saline Agulhas water mixing in along the frontal zone defined by the two water masses (Piola and Gordon,1982). This is verified in that the isopycnal intrusions intensify at stations 61, 62,those closest to the mean position of the Agulhas front (Lutjeharms,1982). This frontal mixing has a large effect on the properties of AAIW,note the salinity increase from 34.29 at AG 61 to 34.41 at AG 62.(Fig.2.4d-e)

The high salinity Sub Tropical water also tends to reduce the

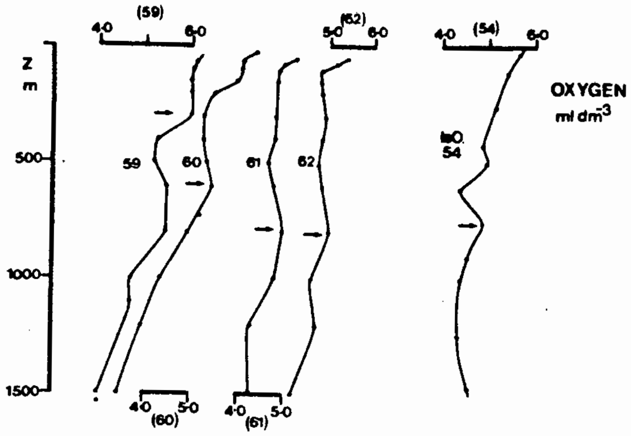
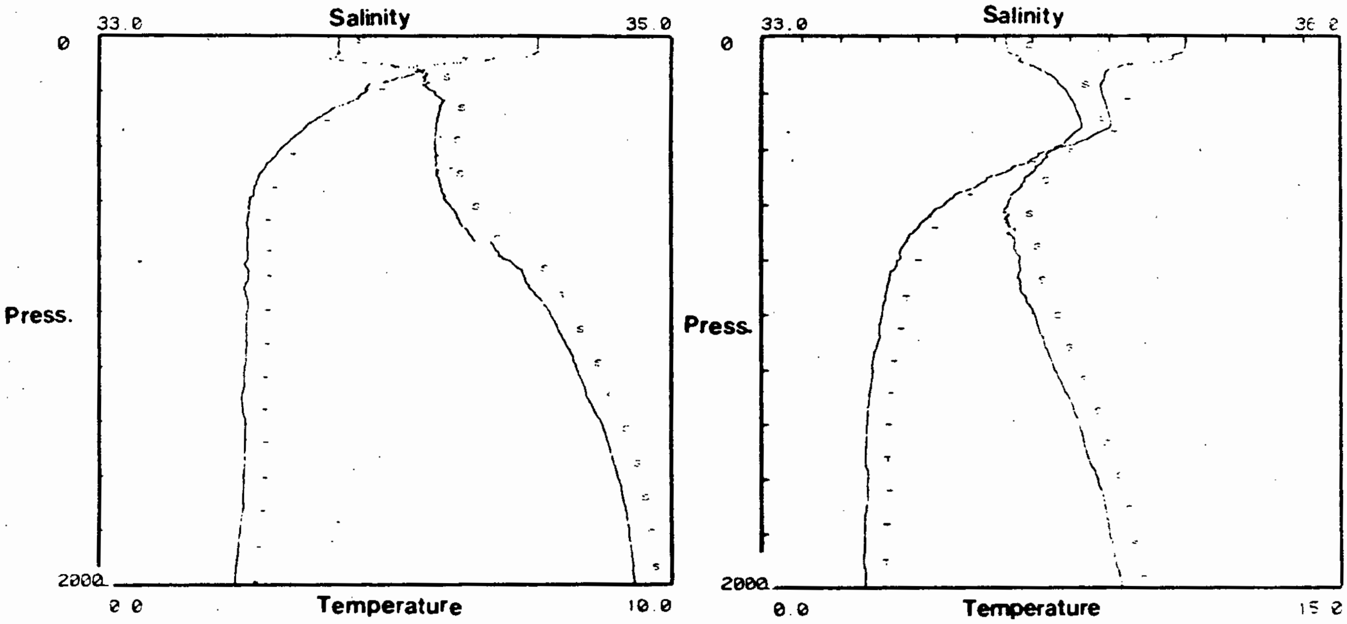


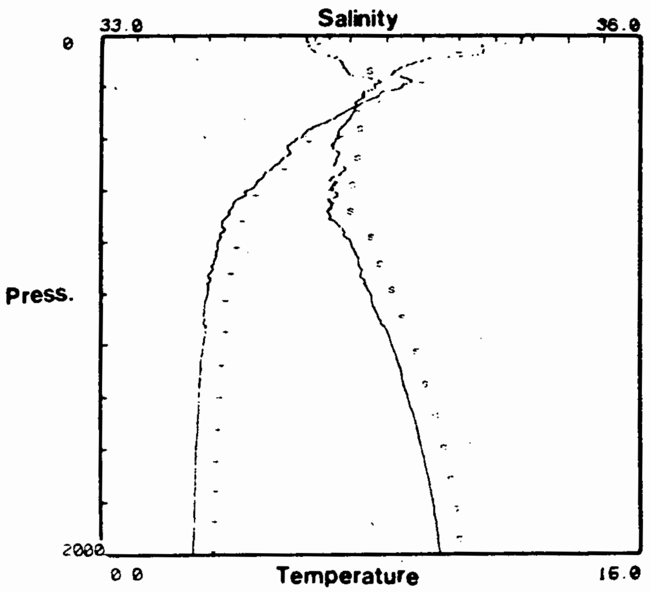
Fig. 2.3 Series of station profiles showing the progression of the oxygen maximum core of Antarctic Intermediate Water.



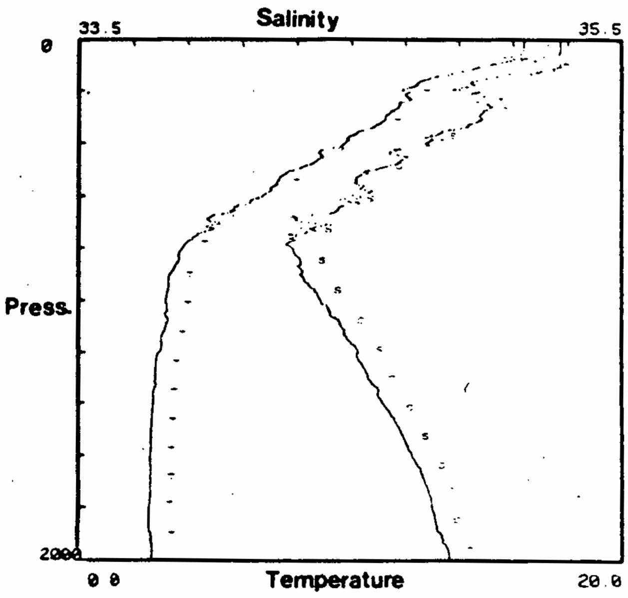
Station AG 58

Station AG 59

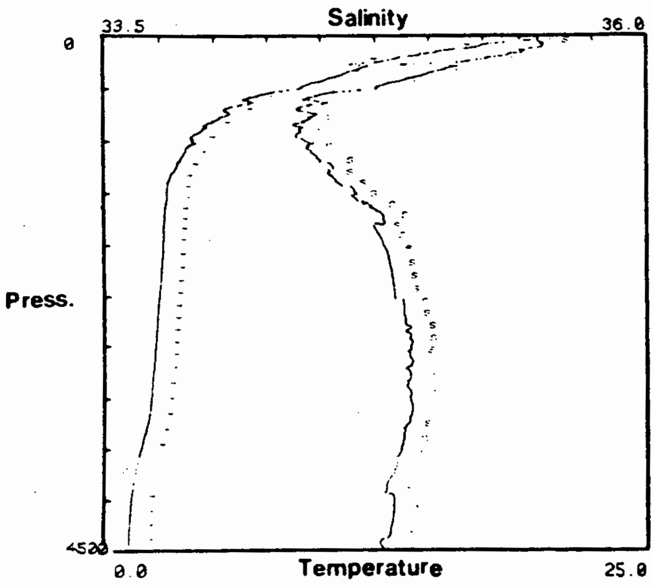
Fig. 2.4 (a-f) CTD profiles from cruise 12 showing the northward change in temperature(T) and salinity(S) structure across the Sub Tropical Convergence.(see text)



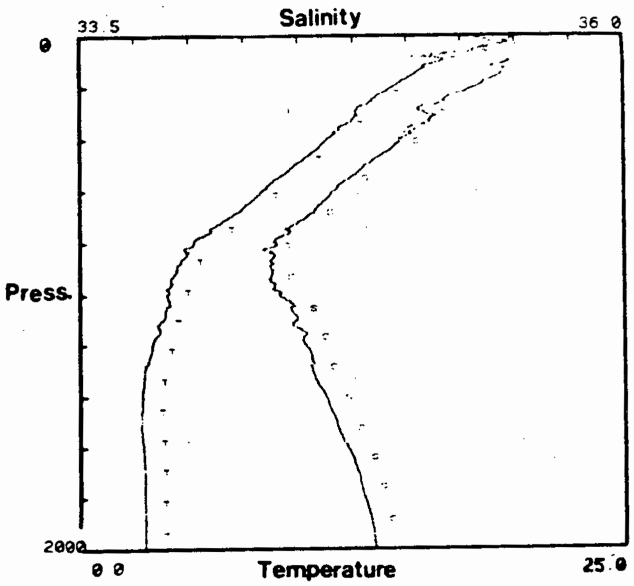
Station AG 60



Station AG 61



Station AG 62



Station AG 63

thickness of the salinity minimum through erosion of its upper layers. This process is observed at station 61 where salinity intrusions of up to $0.1\,^{0}/_{00}$ change the salinity gradient from $3.3\ 10^{-3}\,^{0}/_{00}\,m^{-1}$ at AG 59 to $1.5\cdot10^{-3}\,^{0}/_{00}\,m^{-1}$ at AG 63(Fig.2.4b,f).The oxygen distribution (Fig.2.3) shows the progression of the gross features of the salinity minimum core. There is an erosion of the oxygen maximum associated with AAIW. At AG 59 there is a 200m layer with oxygen at 5.48ml dm^{-3} but at AG 62 this has thinned to 20m and 4.97ml dm^{-3}. The erosion of the upper layers can also be observed by the reduction of oxygen gradient and content from near 6.00ml dm^{-3} to <5ml dm^{-3}. This is consistent with the low oxygen concentration of sub tropical Agulhas waters.(Jacobs and Georgi,1977)

An oxygen profile from the "Islas Orcadas" cruise 12 (station 54) is plotted in Fig.2.3 to compare it with the nearby station AG 62. (Islas Orcadas Reports,1981) The stations were sampled 3 years apart and the station IsO 54 shows an increased oxygen content in the water column above the maximum layer at 700m. This type of result is in agreement with the variable nature of the Agulhas retroflexion region (Lutjeharms,1982) hence confirming the impact of Agulhas water on the properties of SAMW and AAIW.

No salinity minimum core is usually discernable south of the Sub-Tropical Convergence and this is evident when looking at the sections for the "S.A.Agulhas" 18 data Stns AG 9-12 (Fig.2.5a-e). According to the location of the convergence from the XBT section, the sinking of the water should occur just to the north of AG 10. The sigma-T section (Fig.2.5e) shows a well mixed stratum $27.00 < \sigma_t < 27.20$. This is close to the 27.05 value attributed by Wust for 100% AAIW near the surface (Jacobs and Georgi,1977) and it is

Fig. 2.5a-e A series of shallow (0-500m) physical and chemical sections across the Antarctic Convergence(AAC).(cruise18)

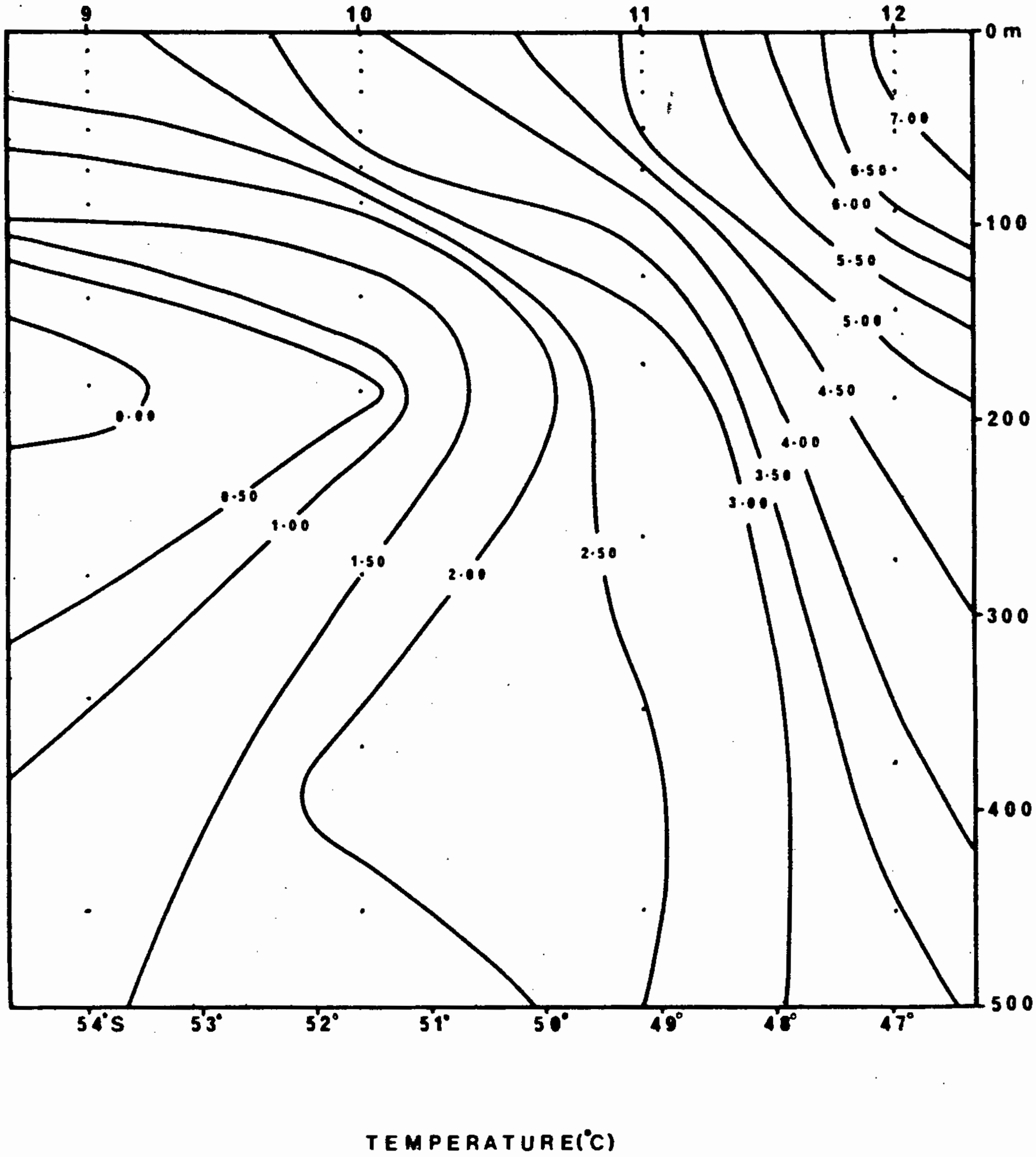


Fig. 2.5a A shallow (0-500m) temperature section across the Antarctic Convergence.

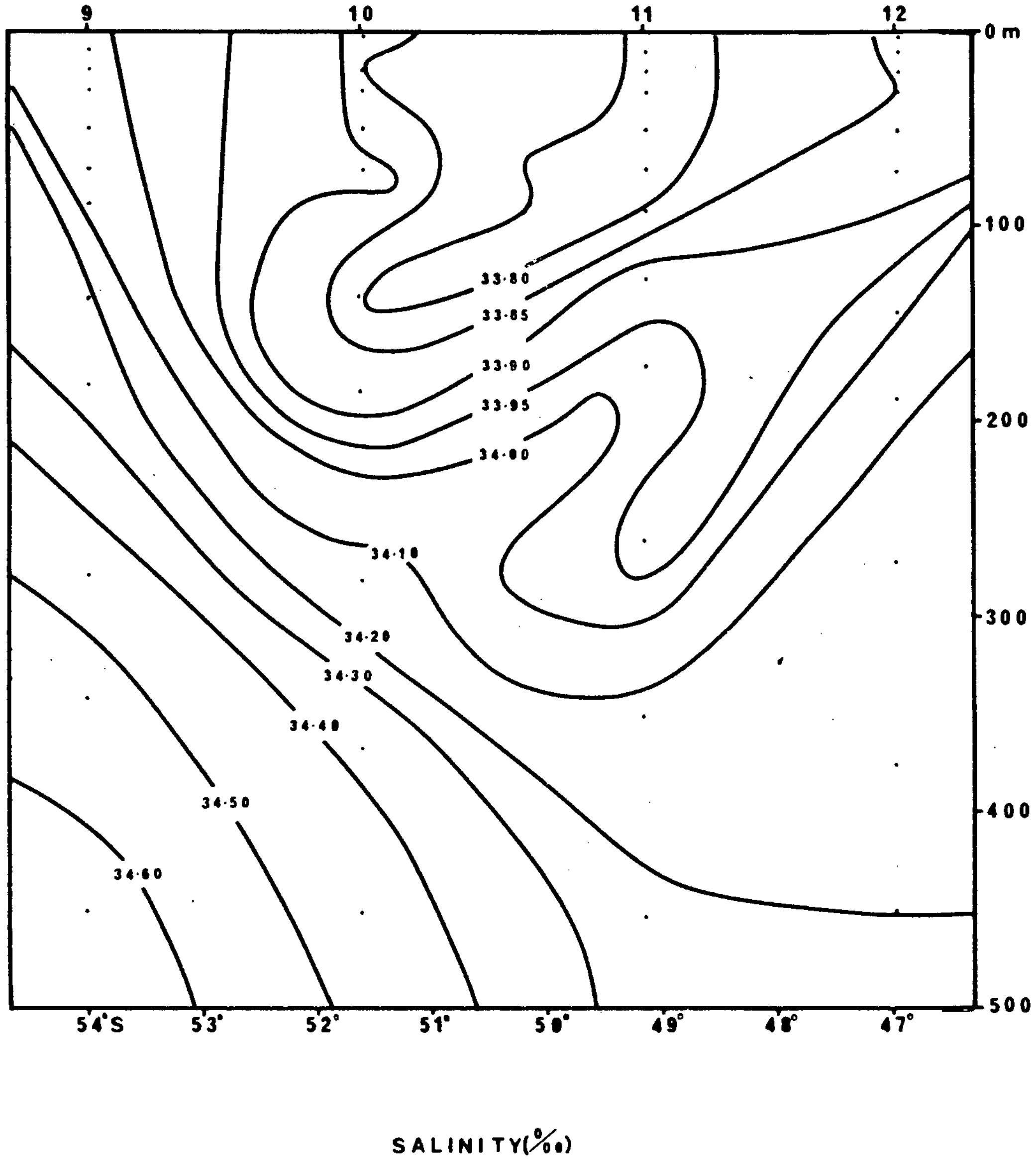


Fig. 2.5b Salinity ^{0}/oo

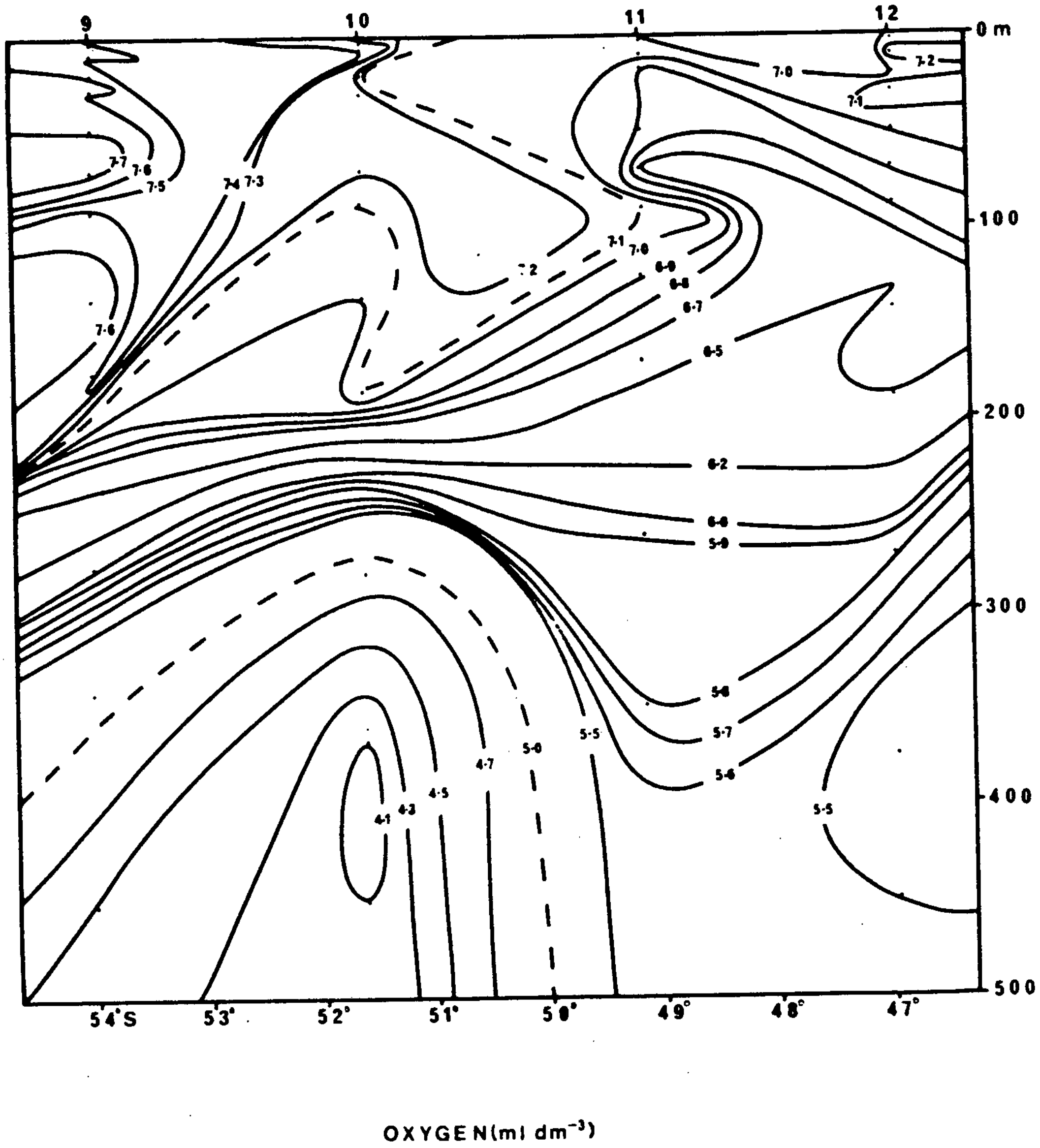


Fig. 2.5c Oxygen (ml dm^{-3})

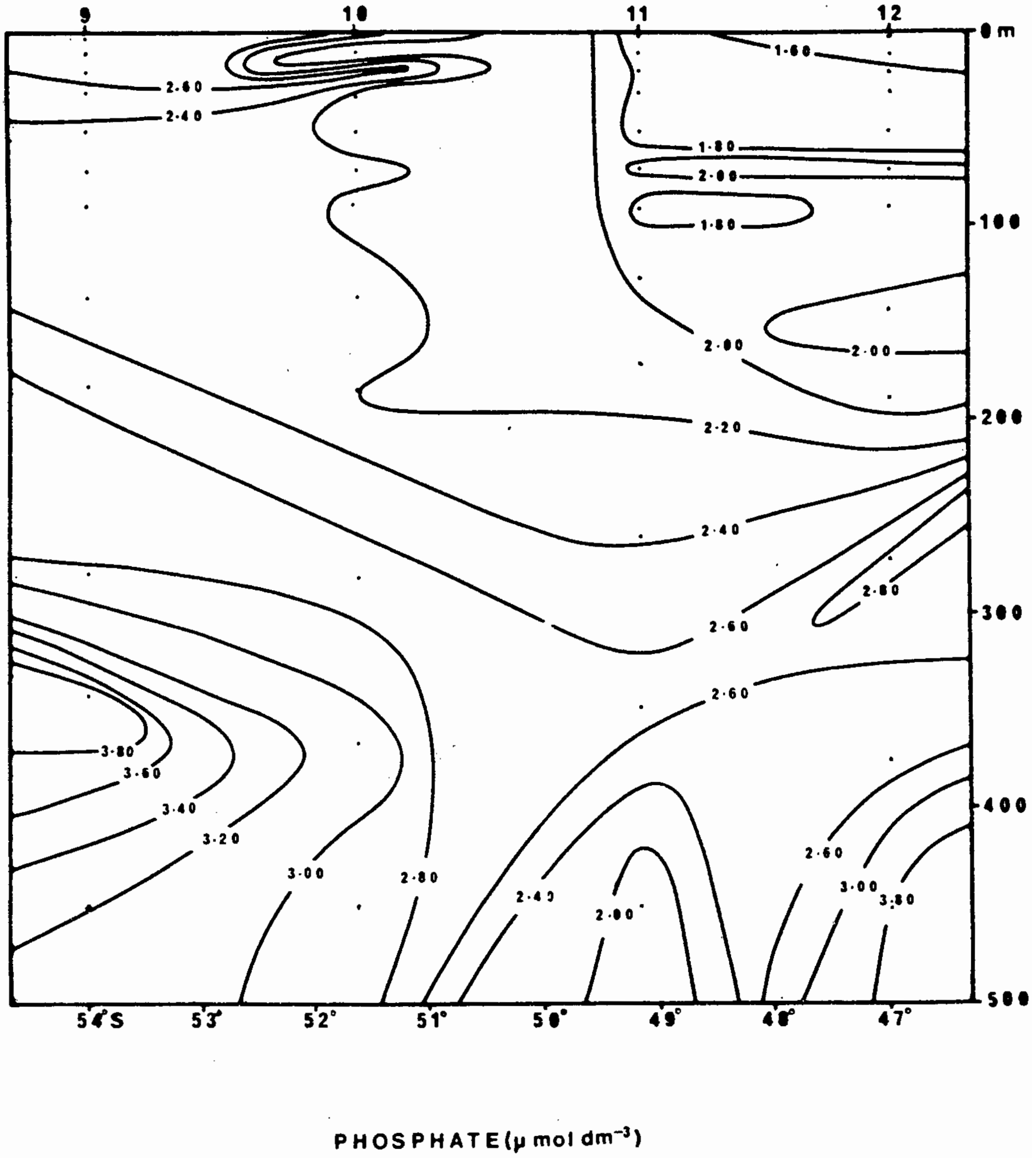


Fig 2.5d Phosphate(μmol dm^{-3})

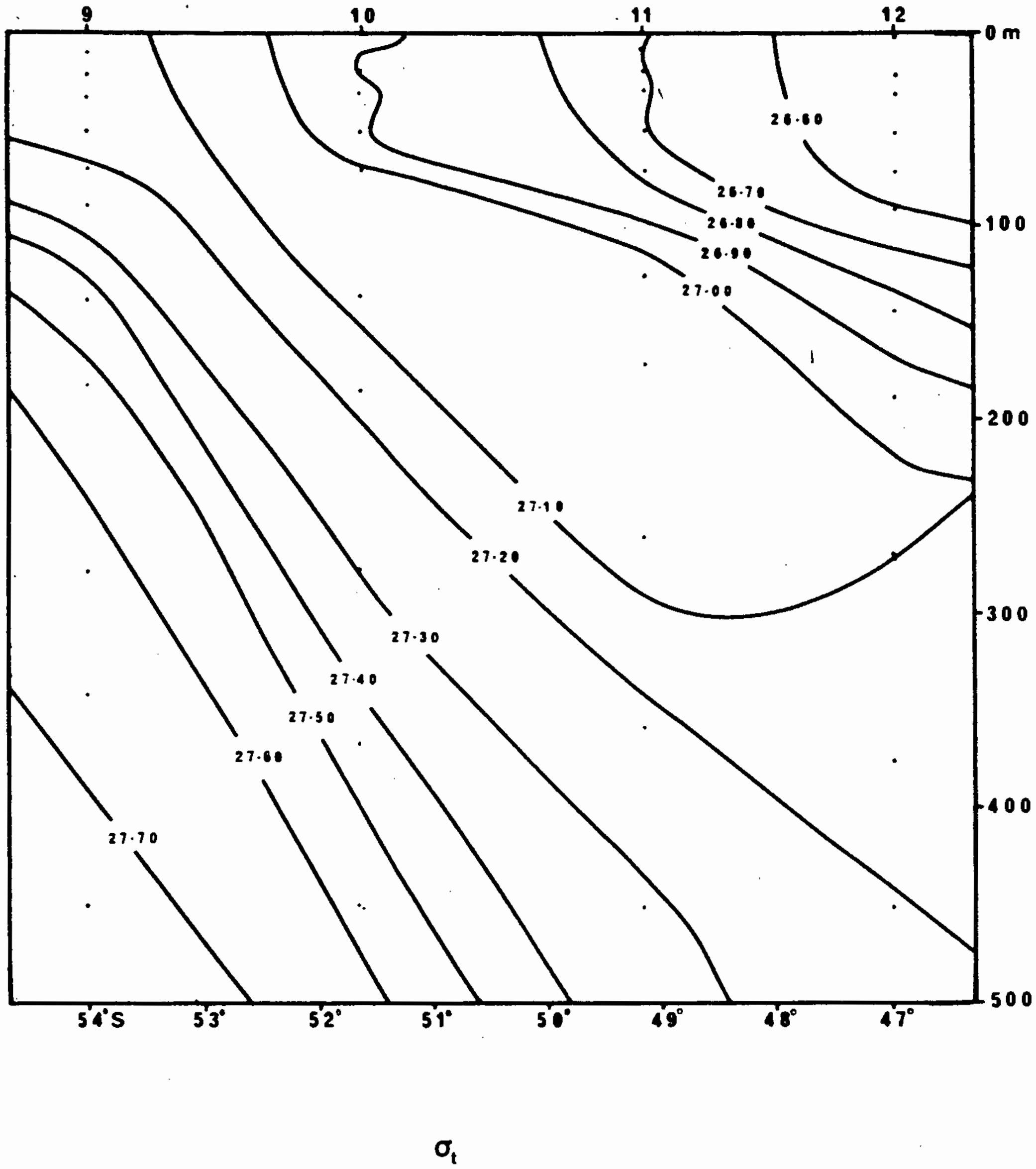


Fig 2.5e Sigma-t (σ_t)

likely that during sinking towards the Sub Tropical Convergence the core properties will be within this sigma-t range. With this stratum defined, inspection of the remaining shallow sections shows a steepening of the isopleths to the north of AG 10. From the salinity section (Fig.2.5b), as mentioned above there is no evidence of a salinity minimum although sinking and extensive mixing characteristic of a frontal zone is clearly seen north of AG 10. The presence of the warm fresh Sub Antarctic Surface Water $S < 34.00$ leads to a monotonic change of these parameters with depth.

The shoaling of the 27.10 isopycnal can be ascribed to intermitent upwelling in the vicinity of Marion Is.(Orren, 1982) The temperature and salinity ranges in this core of water are $2.45< <3.01^0C$; $33.94< S <34.11$ (AG 11) and $3.4^0C< <4.30^0C$; $34.18< S <34.20$ (AG 12). An oxygen maximum is associated with a layer above the salinity minimum of AAIW and careful inspection of the shallow section (Fig.2.5c) shows the development with sinking of an oxygen maximum ($O_2 > 7.1 ml\ dm^{-3}$) to the north of 51^0S. This oxygen maximum forms as the Antarctic Surface Water sinks below the less oxygenated Sub Antarctic Surface Water. The distribution

The distribution of the nutrient elements is complex and can only be interpreted on the basis of an established physical description. The problem is that biological mediation distorts the conservative behaviour of these tracers. In an attempt to evaluate the extent of this effect,a silicate versus salinity plot (Fig.2.6) was drawn; it shows that at stations AG 9-11 the non conservative distribution extends down to approximately 100m. This result was expected since this depth corresponds to the maximum extent of the euphotic layer where uptake occurs, and the

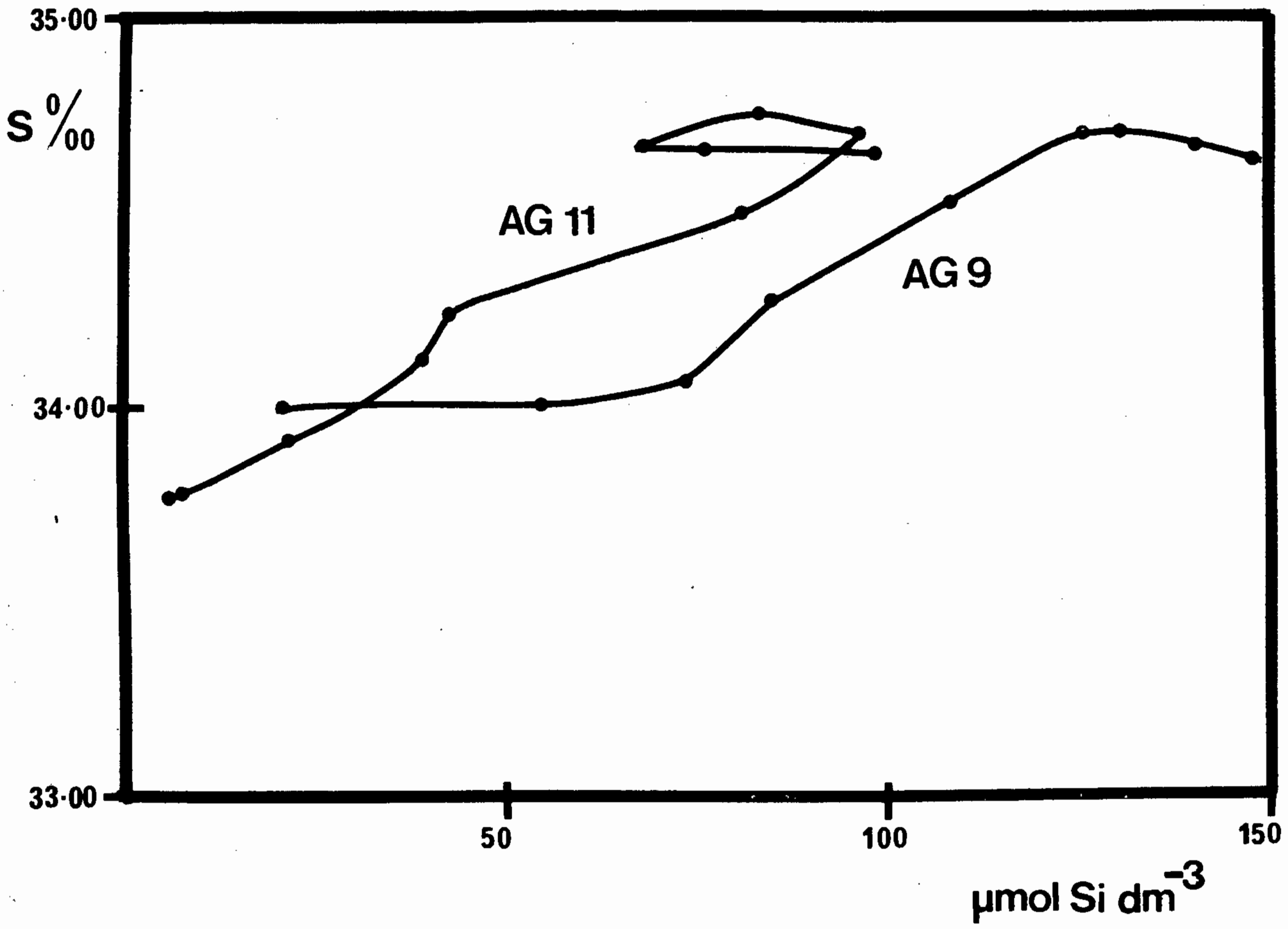


Fig. 2.6: Plot of salinity(S) versus silicate(Si) to show the non conservative behaviour of silicate at the surface and sediment boundaries.

top of the thermocline where decay and accumulation occurs. Below this depth, silicate becomes a useful tracer as borne out by the nearly parallel slopes at all stations. The silicate concentration range associated with the stratum is 20-30μmoldm^{-3}. This is much lower than the Antarctic Surface Water values of 70μmol dm^{-3} hence giving further evidence of a substantial mixing of silicate depleted Sub Antarctic Surface Water. Phosphate concentrations of 2.2-2.6μmol dm^{-3} result in a maximum coincident with the oxygen maximum further attesting to the polar surface origin of the water mass. Though no clear cut conclusion can be drawn from this data, the sections indicate that cross frontal mixing is a dominant feature in the vicinity of the Antarctic Convergence zone.

2.2 Deep Water

The Atlantic-Indian sector of the Southern Ocean exhibits very complex deep water dynamics since this is the confluence region of the three main deep water masses; North Atlantic Deep Water (NADW), Circumpolar Deep Water (CDW) and Weddell Sea Deep Water (WSDW).

Though each water mass can be identified according to its property distribution, (Jacobs and Georgi,1977, Carmack,1977) the mixed zones are not easily resolved since they lie intermediate to the main cores and are often further modified by sinking water at convergence zones. Data from the two cruises,12 and 18 discuss the various characteristics of deep water in this sector.

CHARACTERISTICS

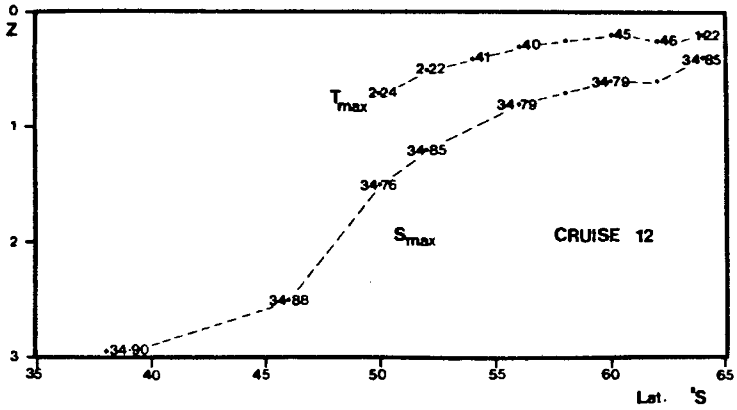


Fig. 2.7 Southward shoaling and convergence of the temperature(T_{max}) and Salinity (S_{max}) cores of Warm Deep Water.

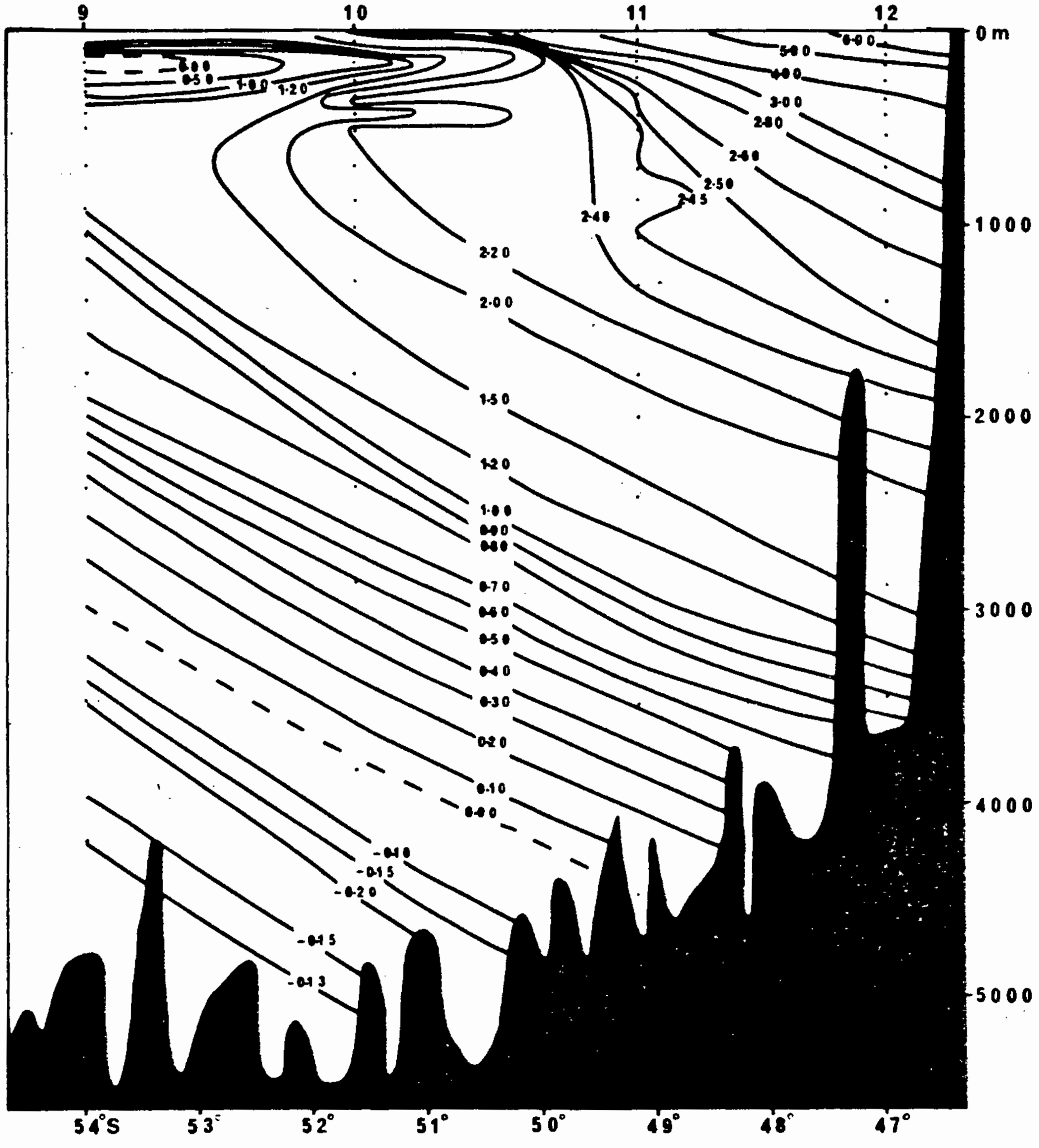
Table 2.1

Lat (^{0}S)	Station	Depth (m)	Oxygen (ml dm^{-3})	Silica µmol dm^{-3}
48^0	54	600	3.74	70.91
50^0	56	800	3.96	63.03
	57	1200	3.91	55.28
46^0	58	1500	4.04	55.69
38^0	62	1500	4.18	45.02

Deep water in the Southern Ocean is broadly characterized by both salinity and temperature maximum cores. (Jacobs and Georgi,1977). Both these cores shoal and converge on one another towards the south to a minimum depth < 1000m at station AG 53 (Fig.2.7). This point represents the zone of shear between east and west flowing currents with resultant divergent Ekman transport. To the south sinking occurs in the vicinity of a continental frontal zone that may result in the formation of Bottom Waters in this region.(Gill,1973) The temperature maximum is only resolved if it underlies the temperature minimum of Winter Water to the south of the Antarctic Convergence. The salinity maximum of 34.91 is at its deepest,3400m, at station AG 62 (Fig.2.4e) which is indicative of the presence of NADW off the south west continental slope of South Africa. The isohalines slope steeply upwards south of the Antarctic Convergence and a strong meridional salinity gradient is seen as the salinity maximum progresses to a lower value of 34.79 at AG 51 (Fig.2.7). The meridional leg of cruise 12 cuts through the Weddell Gyre and to the south of the Weddell Water core T,S values increase as a result of eastward advection of warmer CDW. This is discussed in more detail in the next section dealing with the deep water in the vicinity of the Gyre.

In deep water, oxygen has been found to be a useful tracer as the distribution of this chemical parameter is reasonably well defined for each water mass. An oxygen minimum ($O_{2\,min}$) layer is generally associated with the upper layers of deep water close to the temperature maximum core (Jacobs and Georgi,1977). CDW is advected into the Atlantic through the Drake Passage (Gordon and Rodman,1977) and is characterized by a low oxygen content(< 4.00ml dm^{-3})(Jacobs and Georgi,1977), at a relatively shallow

Fig. 2.8a-e A series of deep physical and chemical sections across the Antarctic Convergence (cruise 18)



TEMPERATURE(°C)

Fig 2.8a Temperature

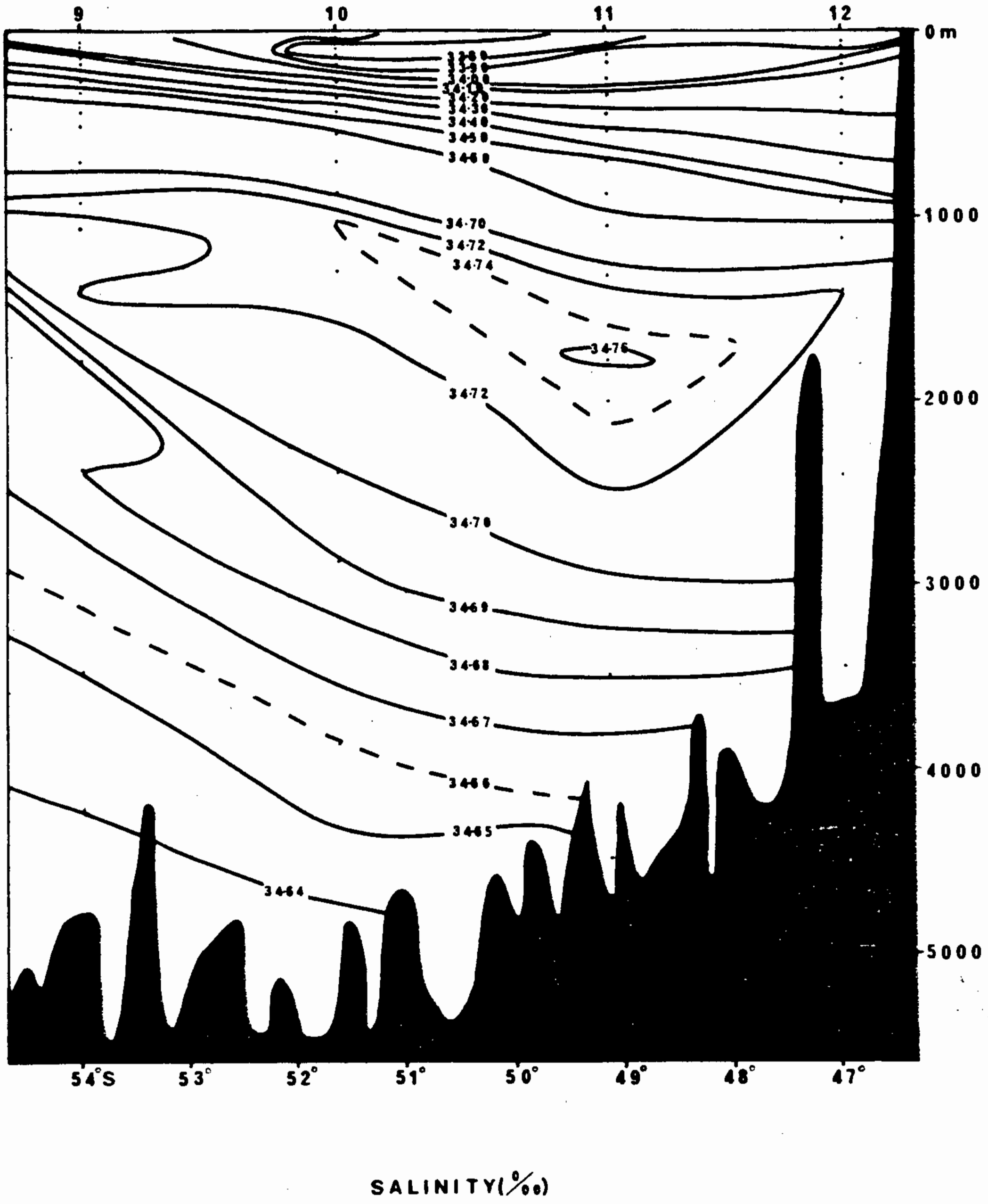


Fig 2.8b Salinity (^{0}/oo)

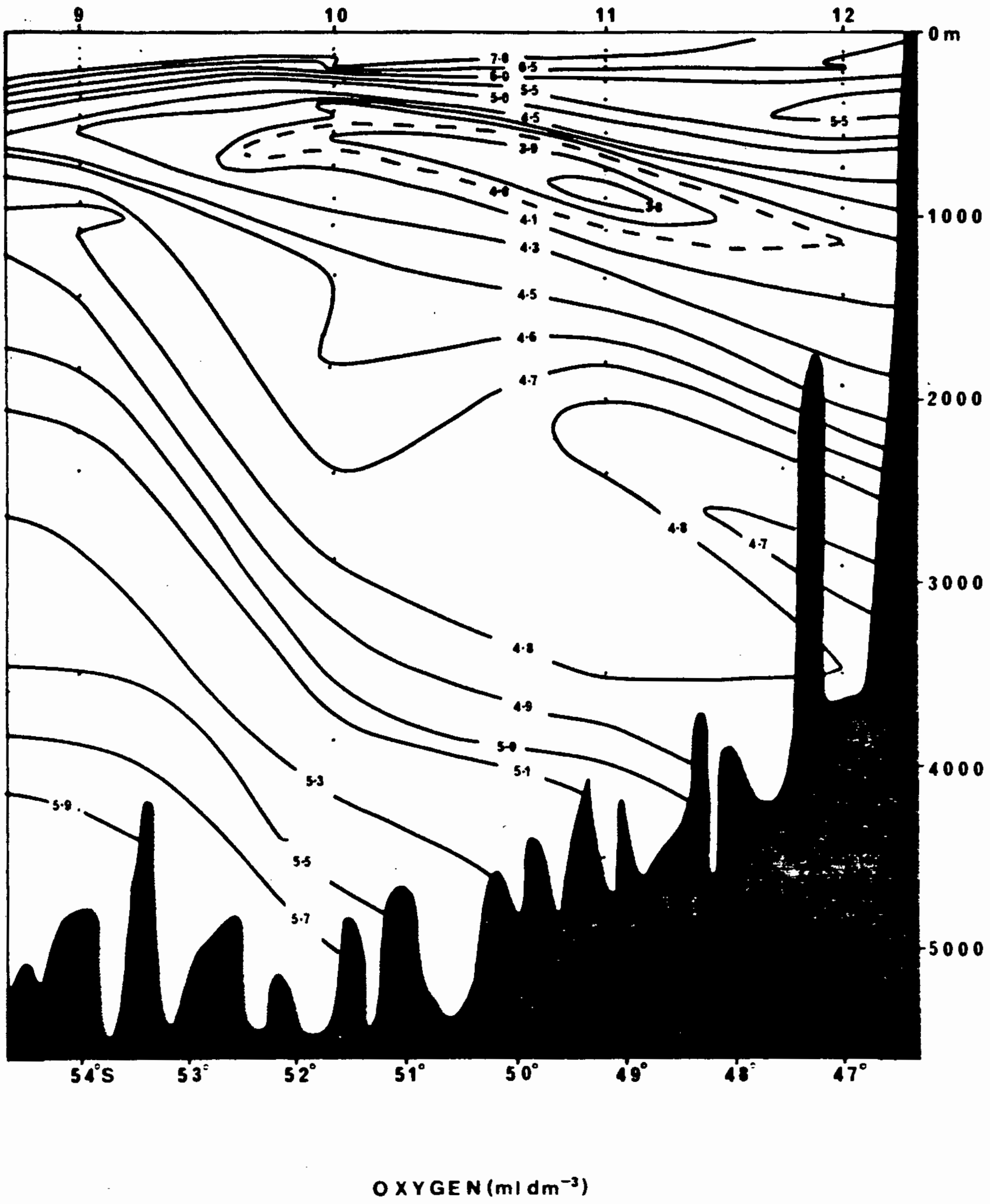


Fig. 2.8c Oxygen (ml dm^{-3})

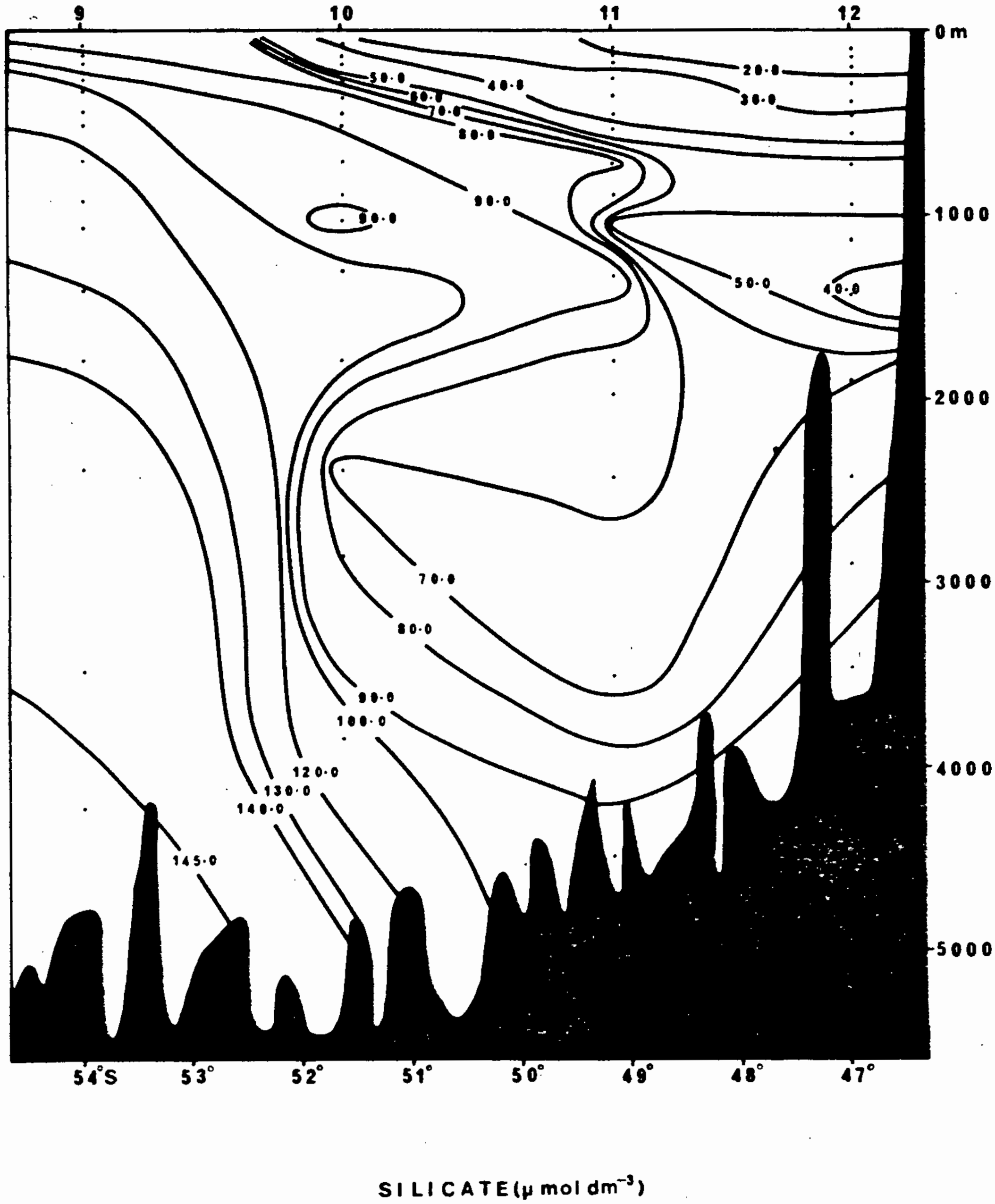


Fig. 2.8d Silicate (μmol dm^{-3})

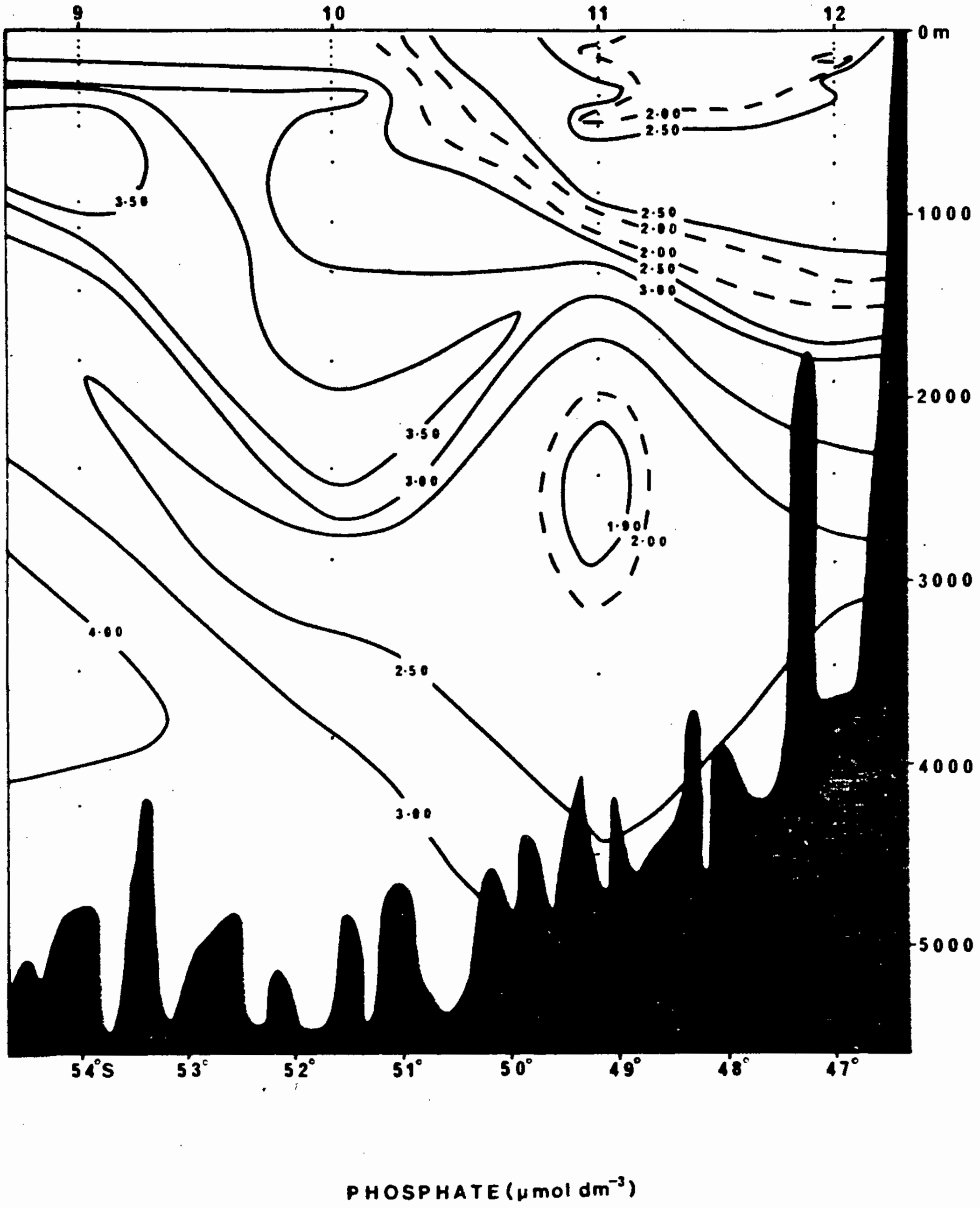


Fig. 2.8e Phosphate (μmol dm^{-3})

1500m. This low oxygen water results from the relatively sluggish circulation in the Pacific Ocean with the resulting lack of ventilation (Edmond,1980), thus the CDW at the Drake Passage should have a large Pacific water component.This result is in contradiction with recent results using neodymium (Nd) isotopic ratios.(Piepgras and Wasserburg,1982).These show that waters from different oceans can be typed according to their ^{143}Nd/Nd^{144} ratio and hence that the Drake Passage water had a 50-70% Atlantic component.The isotope method has not been widely used thus more data is required for this result to be confirmed. NADW is better oxygenated (4.8ml dm^{-3}) thus the bulk of the deep water has an oxygen content resulting from the mixing of these two water mass extremes.

The oxygen minimum coincides with both phosphate and silicate maxima that are characteristic of CDW as opposed to the relatively nutrient depleted NADW. (Gordon and Rodman,1977). The nutrient profiles for cruise 18 (Fig.2.8a-e) show the expected vertical distribution thus allowing water mass assignment to be made. The well defined oxygen minimum, (Fig.2.8c)at 1000m (AG 11), resulting from CDW, increases to 4.8ml dm^{-3} at 3000m with a weakening of the vertical gradients. This weak vertical gradient at the level of NADW (PO_4 $<2.00 \mu mol\ dm^{-3}$; [Si] $<60 \mu mol\ dm^{-3}$) with gradually increased gradients in the upper levels is an indication of mixing occurring due to upward flux of deep water. This 'upwelling' of deep water is consistent with mass balance considerations for deep and bottom water formation and circulation (Warren,1981). South of the convergence zone, in the cruise 18 leg, the distribution of chemical parameters is again very different, showing the presence of a nutrient rich ([Si] $>90 \mu mol\ dm^{-3}$; PO_4 $>3.00 \mu mol\ dm^{-3}$) and oxygenated (O_2 $>4.9ml\ dm^{-3}$) deep water mass(Fig.2.8c-e). The

Fig. 2.9a-e Physical and Chemical sections across the Southern Ocean to a depth of 2000m at a nominal latitude of 10^{0}E.

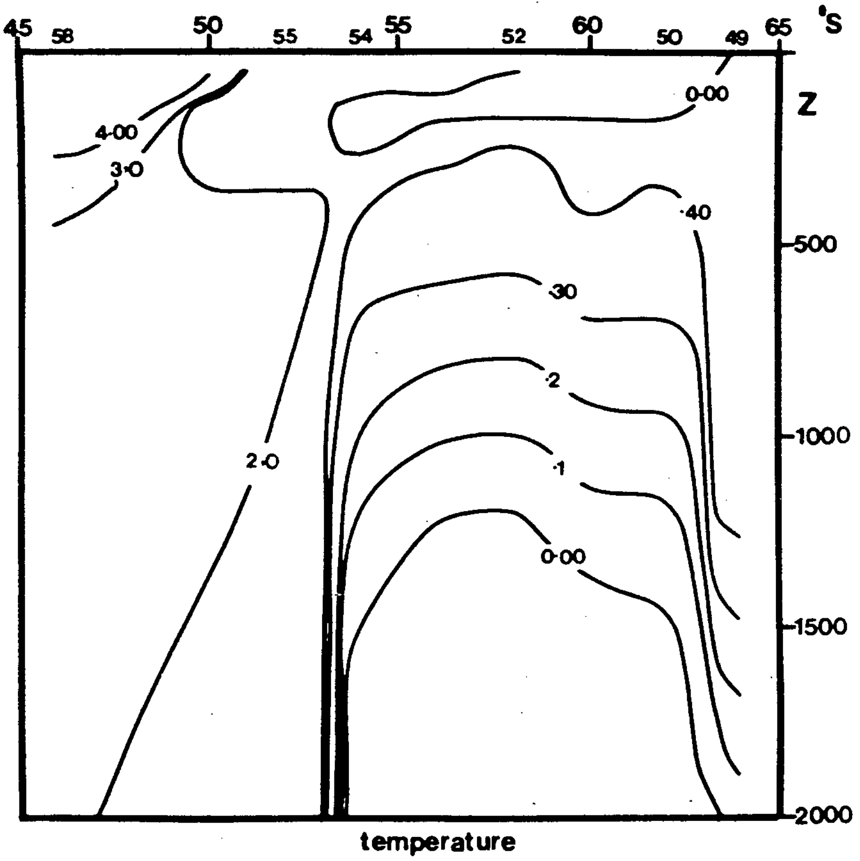


Fig. 2.9a temperature (^{0}C)

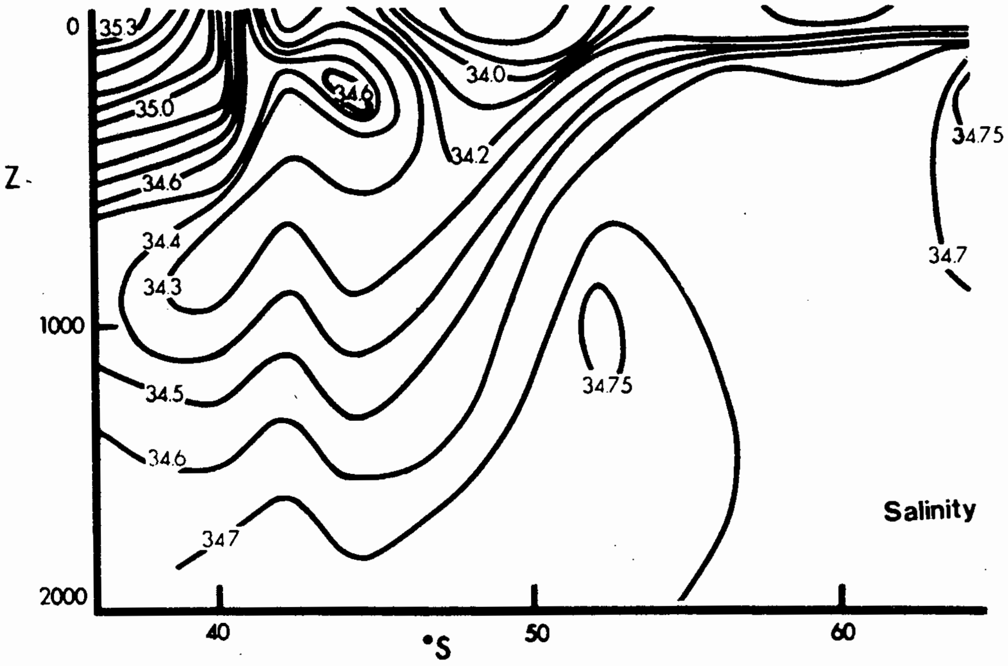


Fig. 2.9b Salinity (^{0}/oo)

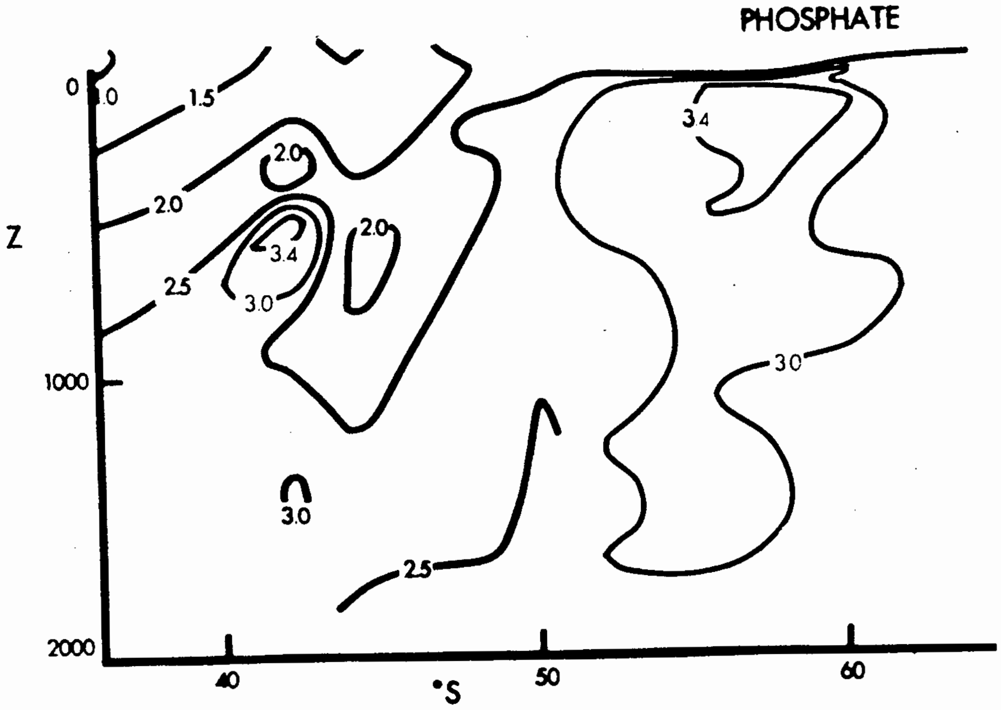


Fig 2.9c Phosphate (umol dm^{-3})

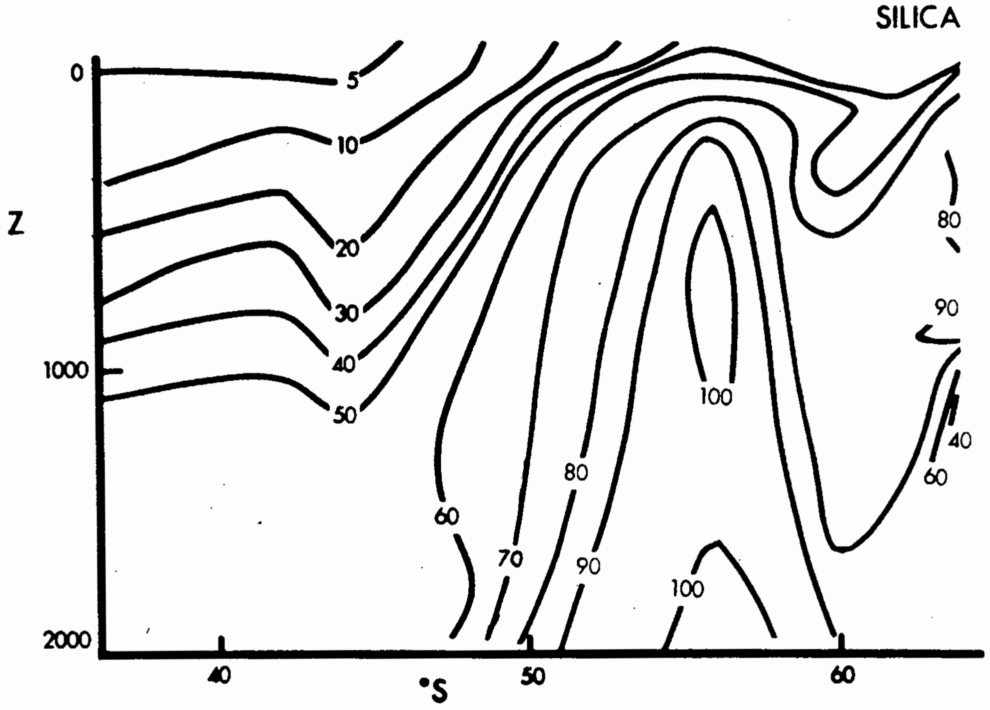


Fig. 2.9d Silicate (umol dm^{-3})

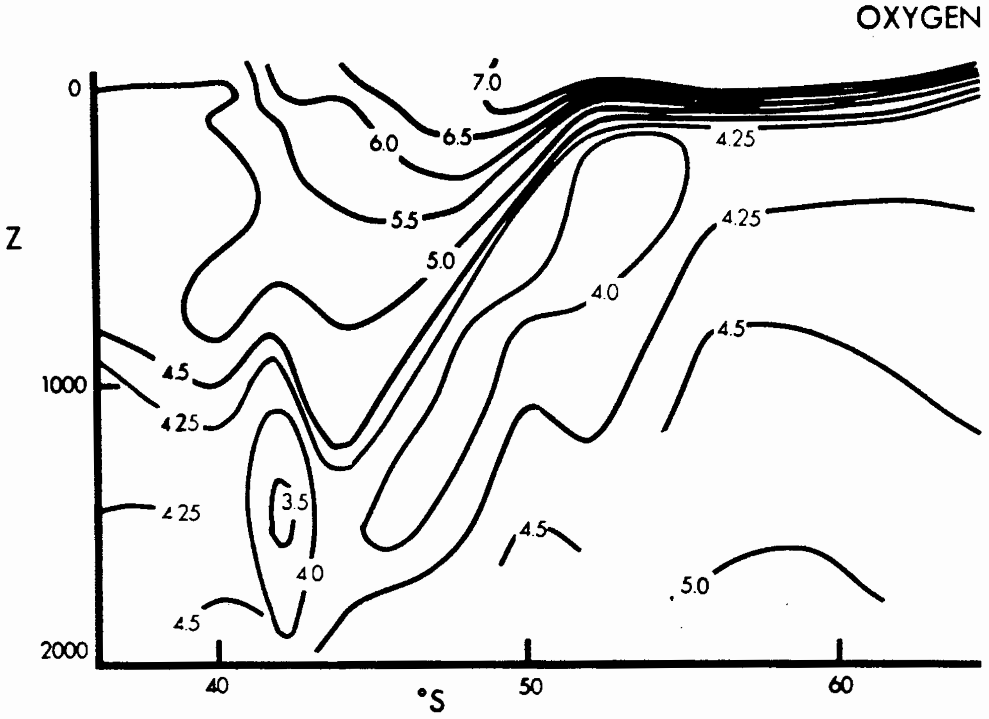


Fig. 2.9e Oxygen (ml dm^{-3})

position of this meridional leg (54^0S; 28^0E) at AG 9 (Fig.2.1) suggests that this is a component of the Weddell Gyre. The characteristics of WSDW are consistent with those found, (Deacon,1979) with the high oxygen content resulting from the relatively rapid ventilation rate of this water and surface exchange due to winter overturning.

On a meridional scale the changes in nutrients are best seen with the data gathered from cruise 12 (Fig.2.9c-e). The relative change of the CDW properties on a meridional section is shown in table 2.1 where the change of silicate at the oxygen minimum is shown.

The northward decrease in silicate is possibly a result of mixing with an increased fraction of nutrient depleted NADW. To the south of 55^0S the oxygen core rises above 4.00ml dm^{-3} (AG 53; 4.14ml dm^{-3}) as a result of the presence of WSDW The presence of WSDW is seen on (Fig.2.9a-e)as a cold, nutrient rich (Si >100µmol dm-3;PO_4 >3.00µmol dm^{-3}),well oxygenated water mass.

2.3 The 2°C discontinuity

At station AG 11(Fig.10a), lying immediately to the north of the Antarctic Convergence, a sharp break in the temperature gradient occurs at a depth of 1300m.This discontinuity in the vicinity of the 2^0C isotherm, results from the mixing of cold, low oxygen, nutrient rich CDW with warmer saline low nutrient NADW.(Gordon and Rodman,1977) The result is a thermostad effect between the 2^0-3^0C isotherms due to cooling of the NADW by mixing of cooler CDW. The

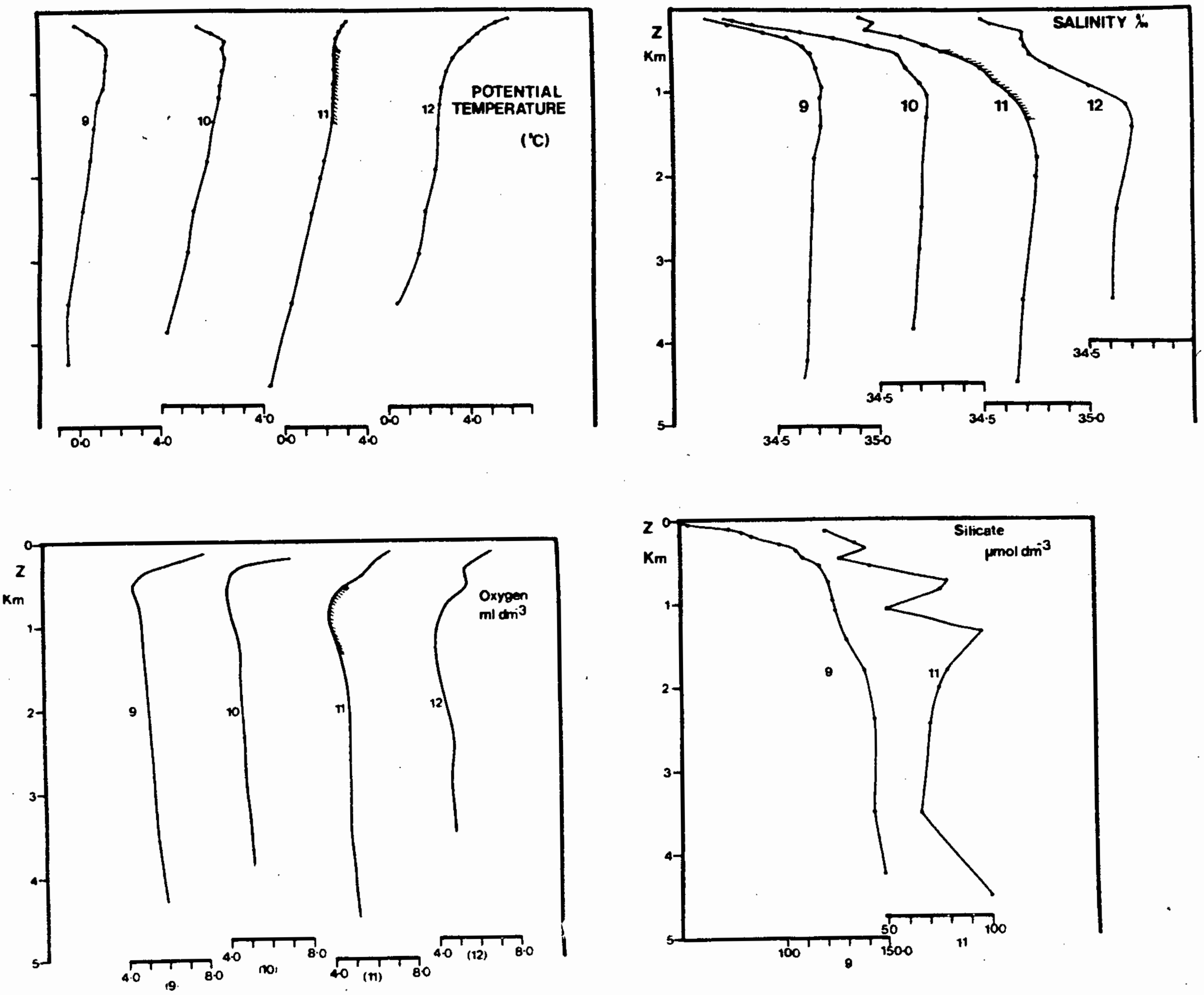


Fig 2.10a-d Serial cast diagrams of stations across the Antarctic Convergence to show the thermostad at the 2^{0}C isotherm(Fig. 2.9a)(shaded region) and the salinity, oxygen andsilicatedistributions at that depth range.

thermostad effect is seen on Fig.2.10a-d. At stations AG 11 and AG 12 a break in the monotonic temperature gradient from the bottom occurs in the vicinity of the 2 C isotherm. The gradient change is:

DEPTH	GRADIENT($\frac{dt}{dZ}$)
2019-1330	8x10-4 ^{0}C m^{-1}
1330-529 m	1.5x10-4 ^{0}C m^{-1}

This corresponds to a factor of 5 reduction in the vertical temperature gradient. The thermostad is stabilized by a large salinity gradient (Fig.2.10b) over the entire depth of the near isothermal water. Other characteristic property distributions are associated with its existence; the vertical oxygen distribution (Fig.2.10c)shows a (3.8ml dm^{-3})minimum at the top half of the thermostad (900m), that is consistent with the advection of CDW through this stratum (Gordon and Rodman,1977).

The oxygen distribution anomaly is best seen by way of $0/O_2$ plots. In non thermostad conditions, the relation between the oxygen maximum should be linear or nearly so,(Fig.2.11). This idealized situation is, however, distorted at AG 11(Fig.2.12) as a result of an influx of cold (near 2^{0}C) water. The dashed line on Fig.2.12 shows the expected relationship, as illustrated at station AG 9 (Fig.2.11). The distribution of the remaining chemical parameters shows a complex pattern that is not so obviously associated with the thermostad (Fig.2.10d). This finding is inconsistent with the prediction of a concomitant 'silicastad' (Gordon and Rodman,1977) but it is possible that these distortions arise as a result of sinking and subsequent mixing associated with the Antarctic

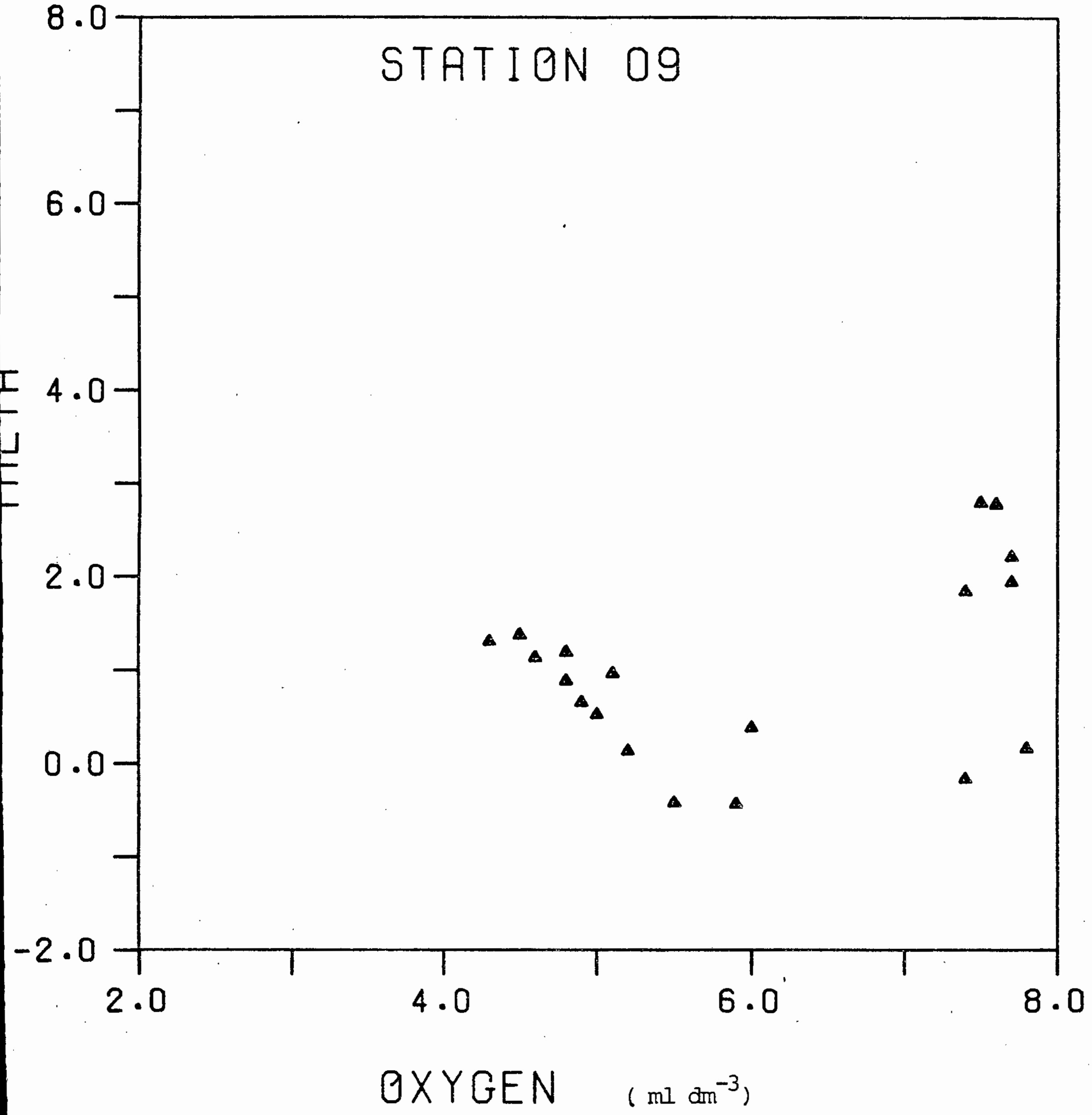


Fig 2.11 Plot of potential temperature versus oxygen at station AG9

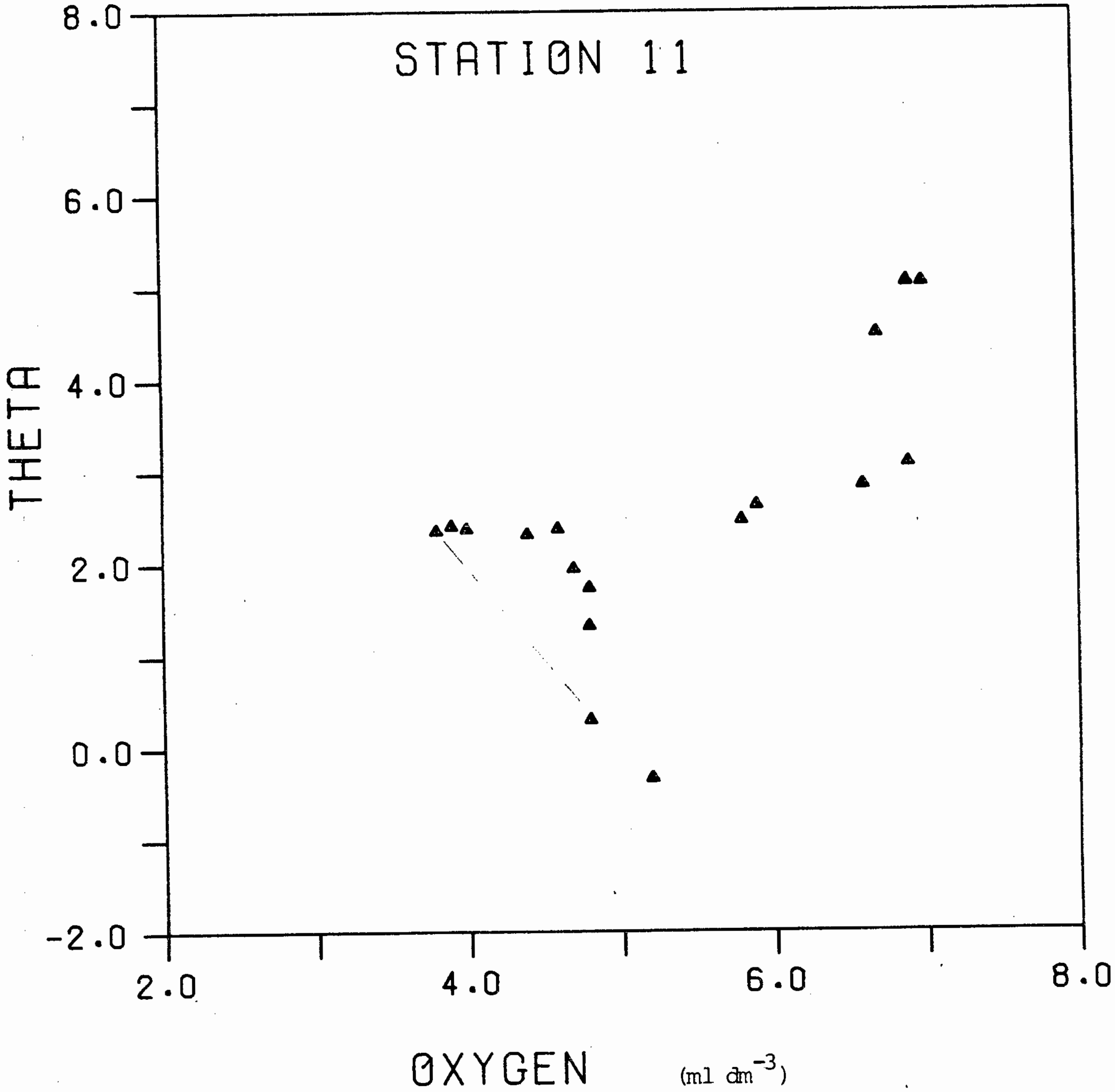


Fig 2.12 Plot of potential temperature versus oxygen at station AG11

Convergence.

2.4 The Weddell Gyre

A number of stations (AG 49-58) were worked along a meridional line, in the course of cruise 12, through the eastern extension of the Weddell drift at 4^0-11^0E.

The wind driven circulation of the Weddell Gyre has been recently reviewed by Deacon (1979) and Gordon et al. (1980).

The temperature section shows a broad(53-65^0S), deep($Z > 2000$m) and cold($t < 1.0^0$C) body of water extending up to 400m from the surface(Fig.2.9a). At its northern limit it is separated from the warmer ($t > 2^0$C) deep water by a sharp frontal zone with a gradient of 10^{-2} ^{0}C/km at 1500m. This front corresponds to the previously defined Bellinghausen front (Deacon,1979) but lies to the south of the sub surface Antarctic convergence found at 50^0S. The slope of the isotherms at the front shows an easterly geostrophic flow but the slopes are not consistent with the slow flow rate of wind driven circulation. This enhanced gradient is likely to arise as a result of upwelling of deep water through divergent Ekman transport to the north of the low pressure centre (Deacon, 1979). The zone of maximum divergent Ekman transport lies to the north of the expected East-West wind shear zone as winds tend to be weak and variable at the centre of the low pressure and to the south. To the north (56-57^0S) the westerly winds intensify with a clockwise wind stress curl which enhance upwelling. To the south the isotherms slope down once more due to the westward component of the Weddell Gyre. The westward advection of warmer CDW is shown by the south frontal zone which is somewhat weaker than its northern counterpart (3×10^{-3} °C km^{-1}). The phosphate and silicate sections (Fig.2.9c-d) show corresponding features that characterize Weddell sea deep water; high silicate >90µmol dm^{-3}; and high phosphate >3.0µmol dm^{-3}. The cross frontal comparisons of nutrient concentrations show the impact of upwelling of WSDW and this process is likely to play a vital role in replenishing nutrients to subsurface waters.

TRACE METALS

Introduction

Though the main interest on trace metals has focussed on their apparent enrichment through the food chain and resulting toxic effects (Riley and Roth,1971), they have had limited application as oceanographic parameters. This problem arises as a result of contamination, usually at the sampling stage (Brewer,1975) which is especially serious when determining at open ocean levels.

Recently however, with the advent of the GEOSECS project, the first systematic trace metal distributions were obtained (Edmond,1980) and determination have improved since then in both accuracy and precision.

This has opened a new field of application for trace metals as water tracers hence making them useful to link physical and biogeochemical processes.

Though very much improved in accuracy, trace metal determinations still suffer from relativelly poor precision which limits their usefulness as parameters for mixing studies. The use of extra independent chemical parameters in a multiparameter mixing model (Tomczac, 1981) requires a natural variability to analysis precision ratio greater than 10**2. The best trace metal analyses are still below this limit.

Little work on subsurface trace metal sampling, has been carried out in the Atlantic-Indian sector of the Southern Ocean. Thus comparison of trends is difficult and most of the features discussed in this work are hypothesised only on the basis of this set of data. The distribution of some trace metals in particulate suspended matter has been investigated (Copin-Montegut and Copin-Montegut,1978; Harris and Fabris,1979) and though some conclusions could be drawn with surface data, at the deeper levels the scatter made interpretation difficult. In the case of the South East Indian work (Harris and Fabris ,1979) this scatter was ascribed to non steady state conditions predominant in the Austral summer.

Trace metals are widely used in the study of biogeochemical processes such as sediment-sea water interface dynamics (Murray and Brewer,1977). Transition series metals are characterized by their significant differences in strucural and thermodynamic properties (Cotton and Wilkinson,1980). These characteristics have an important consequence in any study aiming to model the chemical kinetics of a given system; eg: interstitial water and sediments or the flocculation of colloidal particles in an estuarine environment. Any such model requires the solution of both mass and chemical balance equations which are a function of the uncorrelated variables available. The nature of the binding sites on the particulates suspended in the water column and in the sediments is also crucial in dictating the stability of the resulting complexes. The binding ability of inorganic particulates usually associated with sediments is given as

MnO_2 >> FeO.OH >> deep sea clays > illite > montmorillonite > kaolinite

(Simpson,1981). The above order ignores the effect of particulate organics or organic films; these would also be important in considering geochemical equilibria especially in the case of copper whose organic complexes are very stable.

The elemental ratio changes, are discussed in particular in the ensuing discussion.

Copper

Surface and subsurface

The concentration of copper in this depth range shows a great deal of variability, but all stations in the Antarctic zone show a similar enrichment with depth.

The vertical profile at station AG 5 is shown on Fig. 3.1 where the near surface depletion (1-1.5 nmol kg-1) increases sharply along the pycnocline to copper concentrations exceeding 2.0nmol kg-1.

This type of subsurface vertical structure is most likely a result of biologically mediated processes which predominate in this depth range because of:

1. Euphotic layer
2. Stable water column at the top of the pycnocline.

Copper at low concentrations is an "essential" element for primary production (Riley and Roth,1971). At the concentrations found in these waters, copper is expected to respond as do other nutrients to a transfer from the dissolved species to the particulate

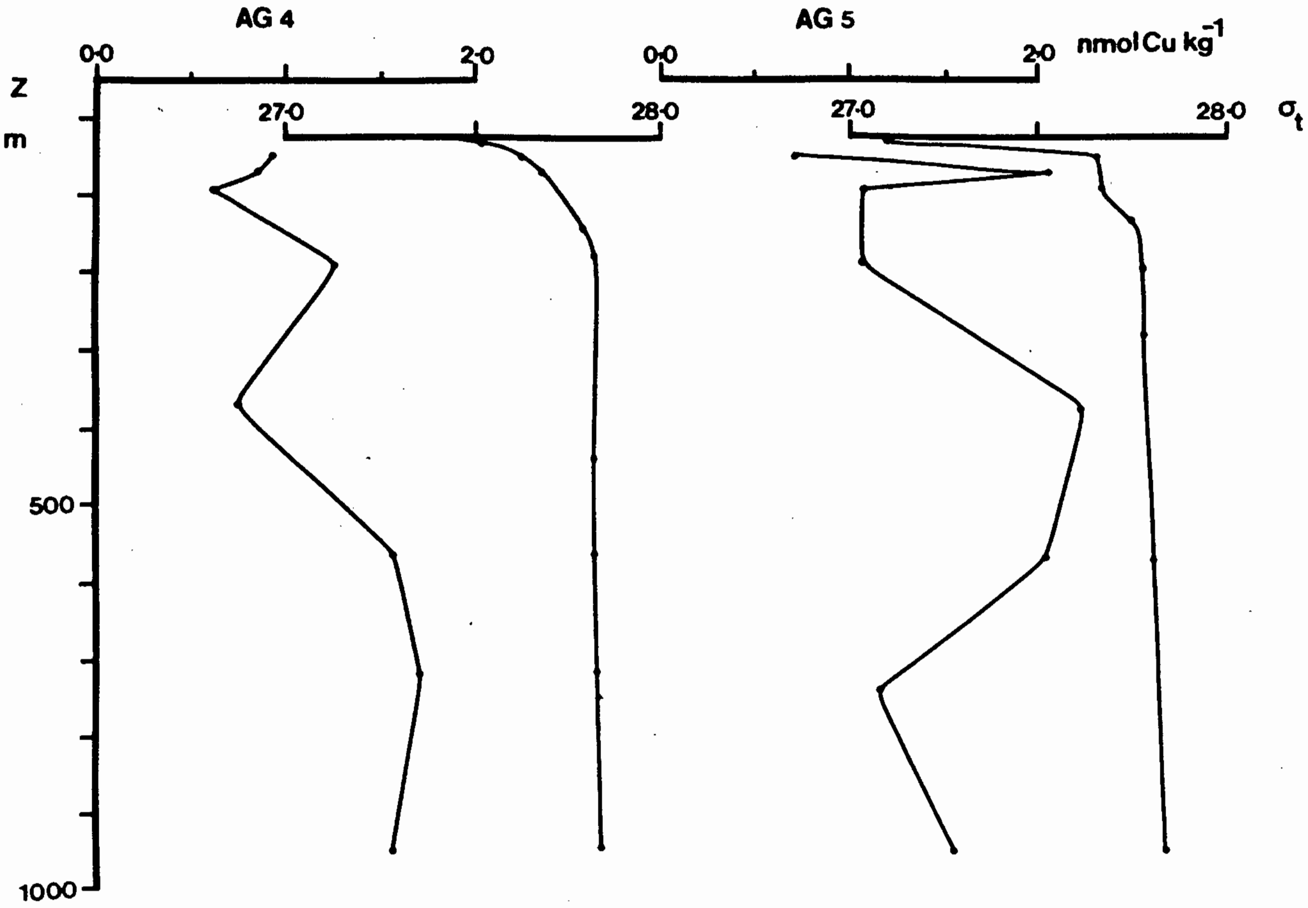


Fig. 3.1: The vertical distribution of copper and sigma-t at stations AG 4 and AG 5 in the Antarctic zone. The copper profile near the surface appears to be closely linked to the pycnocline.

organic phase. The senescent and scavenged organisms undergo a process of physical and chemical degeneration, and the chemical components distribute among the species characteristic to the governing conditions. These equilibrium reactions, in particular absorption and desorption, usually dictate the mechanism and rate of removal of the chemical components from a given system (Murray and Brewer,1977; Simpson,1981). The various types of sorption equilibria between different particulate phases and some of the chemical components(eg. Zn, Cu, Cd and Si)will result in changes in the ratios of these components, and an attempt is made to investigate some of the processes in the water column using the ratio of copper to silicate(Cu/Si). These components are felt to have been the most reliably analysed.

The distribution of copper and sigma-T for two stations (AG 4-5) are given on Fig.3.1.The density profiles show that two distinct pycnocline modes exist:

1. Seasonal: characterized by the large gradient due to simultaneous melting of ice and warming from incident solar radiation.

2. Permanent: weaker gradient as salinity change with depth is the stabilizing factor.

The process of vertical transport of biogenous particulates has the rate determined by the viscosity coefficient and the density difference between the particle and the sorrounding water.(Komar et al.,1981)

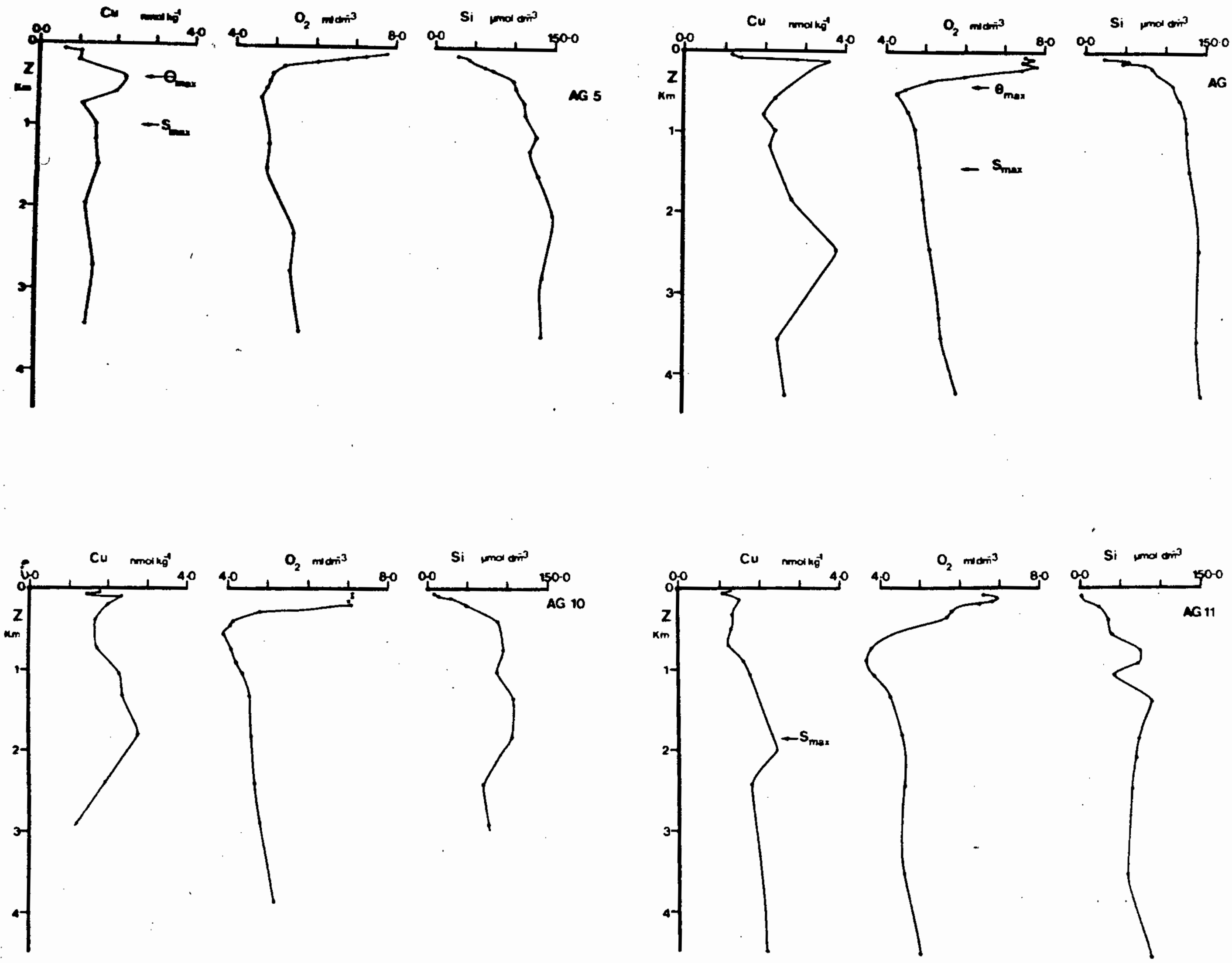


Fig. 3.2: Vertical profiles of copper(Cu), oxygen(O_2) and silicate(Si) at a number of stations whose positions are shown on Fig. 2.1.

These two effects work together to slow down the rate of settling thus resulting in most of the chemical components being released in the upper layers. Work carried out in the Southern Ocean, south of Australia (Harris and Fabris,1979) showed an accumulation of total suspended matter and particulate organic carbon(POC) in the upper 100m of the water column.

As shown on Fig. 3.2a, copper and silicate have similar systematics in that both show an increase with depth over the top 500m of the water column. The gradients are shown to vary from station to station reflecting the variable production rates and advection of sub surface water by upwelling. The data shows further that copper and silicate correlate well in this depth range which indicates that as expected(El-Sayed,1977),diatomaceous primary producers dominate the planktonic species.

The silicate gradients with depth extend to a greater depth than copper (Fig.3.2a-d) which indicates that copper redissolves faster than silicate. This result suggests that copper is predominantly associated with the organic "soft tissue" rather than the opaline tests.This is consistent with the finding by Boyle and Edmond, (1975) that surface copper concentrations south of Australia correlated well with nitrate values. (The nitrate data from cruise 18 was found to be unreliable and discarded.)

This is a region of intense upwelling as discussed in chapter 2.1 thus the surface waters would be mixed with the upwelled silicate rich deeper water.

The northern leg of stations does not show such a predictable correlation but it appears that the lower silicate values make this element more likely to be limiting in the case of a high demand.

This is especially so to the north of the Antarctic Convergence where the low silicates in surface waters of less than 10 umol dm-3 (AG 11).

The copper concentrations fall within the range found within similar zones, south of Australia (Boyle and Edmond,1975) where it was found that Antarctic surface waters were enriched in copper relative to tropical waters. A survey of the literature covering tropical and sub tropical waters does not confirm this finding (table 3.1).

The surface water data taken from a depth of 50m, shows little meridional pattern (table 3.2) in the case of copper although the silicate values drop sharply across the Antarctic Convergence.

This silicate drop indicates the presence of Sub Antarctic Surface Water but it does not appear that copper is similarly depleted. It is interesting to note that the lowest copper concentrations in this surface data are found in the cores of Winter Water(t < 0.0). where the highest silicate concentrations are found. The explanation for this result may lie in the process of winter freezing that gives rise to this cold water.

Table 3.2

The meridional distribution of copper and silicate in surface waters in the Atlantic-Indian sector of the Southern Ocean.

Nominal Latitude	Station	Temperature (°C)	Salinity °/oo	Copper (nmolkg^{-1})	Silicate (µmoldm^{-3})	$\frac{Cu}{Si}$
68°S	4	-1.49	34.35	0.92	69.0	13
67°S	5	-1.39	34.37	0.68	70.4	9
54°S	9	2.20	34.01	1.34	54.6	24
52°S	10	3.87	33.86	1.79	7.5	238
49°S	11	5.05	33.78	1.40	6.5	215

table 3.3

Copper and cadmium concentrations in interstitial waters of bottom sediments in the Atlantic Ocean.

Position	Station	Water Depth	Sediment Type	Cu	Cd
		m		µg dm^{-3}	
62°58'S/28°52'E	K	5239	Siliceous ooze	10-52	0.2-0.8
64°41' /29°53'E	L	4957	Siliceous ooze	11-62	0.1-1.5
58°56'S/33°32'E	o	5292	Siliceous ooze	14-32	0.5-2.1
40°46'S/34°26'E	T	4919	Clay sediment	20-36	1.0-2.6
33°07'S/31°57'E	V	3657	Calcareous ooze	13-42	0.3-2.4

to this cold water.

This result is not necessarily in contradiction with the study in the South West Pacific (Boyle and Edmond,1975) as such factors as biomass production and sampling zones can render comparisons difficult.It stresses however, that models created on the basis of data from a given location cannot simply be extended elsewhere.

The overall near surface data gives a Redfield ratio for Cu/P of 0.50×10^{-3} that differs from the Boyle and Edmond(1975) value of 1.7×10^{-3}. The plankton ratio has been given as 6.6×10^{-3} (Boyle and Edmond,1975) and this discrepancy can be ascribed to:

1. Region to region variability according to local physical and chemical conditions and planktonic species.
2. Enrichment of copper in the organic milieu of plankton due to its high stability with organic binding sites also reflected by its position in the Irving-Williams series.

There has been some evidence that the Redfield ratio shows deviations from the expected values in the Southern Ocean(Chesselet,1982). but further study is required to confirm this result.

Deep and Bottom waters

In this context deep and Bottom water are defined as lying below the copper maximum at the lower end of the main pycnocline(Fig.3.2a-d).

In the deep section of the water column, far removed from any biogeochemical source or sink , the chemical tracers would be expected to reflect a more conservative distribution, possibly characterizing a local water mass. As is further dicussed below, it was found that a consistent minimum at all stations was a property core of CDW. However, nearer to the bottom, a non steady state situation arose ,which was ascribed to the interstitial water flux into overlying AABW.

The primary question that has to be assessed is: Does the vertical distribution of copper at a given station arise from local (biogenous) or advective processes ?

Emphasis will be placed on stations AG 9-11 - the physical processes of this zone have been discussed in chapter 2 - but the remaining data will also be used.

The copper profiles of stations AG 9-10 (Fig.3.2b-d) show a mid-water minimum below the subsurface maximum, in the vicinity of the oxygen minimum and lying between the temperature and salinity maxima. The oxygen minima (O2 < 4 00ml dm^{-3}), -(section 2.2)- arise due to the advection of Pacific CDW into the Atlantic Indian sector. This would suggest that the copper minimum of less than 2.00nmol kg^{-1} is also a characteristic of this water mass.

The copper minimum layer is observed to extend the southerly group of stations as at AG 5 (Fig.3.2a) where together with the oxygen minimum, it also lies between the temperature and salinity cores. Here it appears as a sharper minimum with lower magnitude (1.17 nmol kg^{-1}) and an oxygen minimum of 4.68 $mldm^{-3}$.

There does not appear to be any local source of water with these characteristics thus, lateral advection and mixing seem to be the most likely possibilities.

The copper minimum in CDW has not been reported previously in the literature, and to further verify this it would thus be necessary to work stations in the vicinity of the Drake Passage.

Below the minimum the vertical profile shows an increase to a maximum (Fig.3.2a-d) where a sharp break marks a decrease to the bottom. The deep break at 1400m at station AG 5 and 2400m at AG 9,10 is a recurrent feature and is always found near the salinity maximum core. This core has been used to define the lower limit of Warm Deep Water (Jacobs and Georgi,1977). The increase of copper in Deep Water follows the silicate increase and has been observed in the Indian Ocean (Danielsson,1980), Atlantic Ocean (Bender and Gagner,1976) and Pacific Ocean (Edmond,1980). It would appear that this is a characteristic of a northern source of Deep Water intruding between two water masses (CDW and AABW) formed in the Southern Ocean.

The low copper content of AABW can only result from the mixing of end members also depleted of this metal. This is consistent with the observation that CDW has a low copper content.This result is important in the ensuing discussion where it is shown that the silicate enrichment in AABW is accompanied by a concomitant increase of copper.

Newly formed bottom water has been found to be depleted in silicate relative to overlying deep water (Edmond et al.,1979). This is observed at station AG 5 (Fig.3.2a). Further north the silicate distribution shows a strong maximum towards the bottom at AG 9.

The silicate enrichment within the bottom water strata could be ascribed to one of two probable mechanisms:

1. A flux of interstitial water from the siliceous abyssal sediments resulting from the gradient set up between the silicate rich interstitial water and bottom water.

2. A surface derived input from the dissolution of falling biogenous particles;especially faecal pellets.

Of these two hypotheses, the first one, of an interstitial water flux,is favoured in view of the high silicate concentration of interstitial waters (Edmond et al.,1979; Manheim,1976). Though measurements have been made of radioactive isotope fluxes from sediments (Rn^{222}, He^{3}) to quantify the eddy diffusion coefficient values (Broecker,1981) there is in fact no direct evidence of an ion transport flux from sediments (Manheim,1976). It is hoped that the data acquired in this region will show, by means of the Cu/Si ratio that a bottom input is indeed the only mechanism that would justify the results. This approach, of elemental; ratios has been widely used to characterize given geochemical processes (eg: Redfield ratio) and was used by Dittmar (Manheim,1976) to show that the Ca/Cl ratio implied a bottom dissolution of Calcium into the water column.

The copper data for interstitial water in South Atlantic sediments was obtained in the course of an "Eltanin" cruise and sampled by a Sayles type probe (Orren,1982). The data gives the interstitial water concentration ranges over the top 100cm for copper and cadmium(table 3.3):

On the basis of a Bottom water copper concentration of 0.5g/dm^{-3} (7 75 nmol dm^{-3}) the copper flux was found to be 7.1 x 10^{-16} g/cm^{2}/s (Orren,1982). In the concentration gradient term of equation 1

$$\frac{dc}{dt} = k\,\frac{dc}{dZ}$$

the critical value is the concentration of the chemical component in the interstitial water as it is an order of magnitude higher than the Bottom water concentration.

Values for the silicate concentration in interstitial waters at the same station as the copper ones were unavailable.Thus on the basis of work done in the North Atlantic (Schink et al.,1974,1975), this value was estimated as 500 mol dm^{-3}.For the purposes of this calculation the exact figure is not crucial as one is looking only at orders of magnitude. From this data the Cu/Si ratio of interstitial waters was calculated as 900*10-6. Comparing this result with that typical of AABW, one expects a net copper flux out of the sediments .(table 3.4) Thus the enrichment factor of copper to silicate from AABW to interstitial waters is about 50.

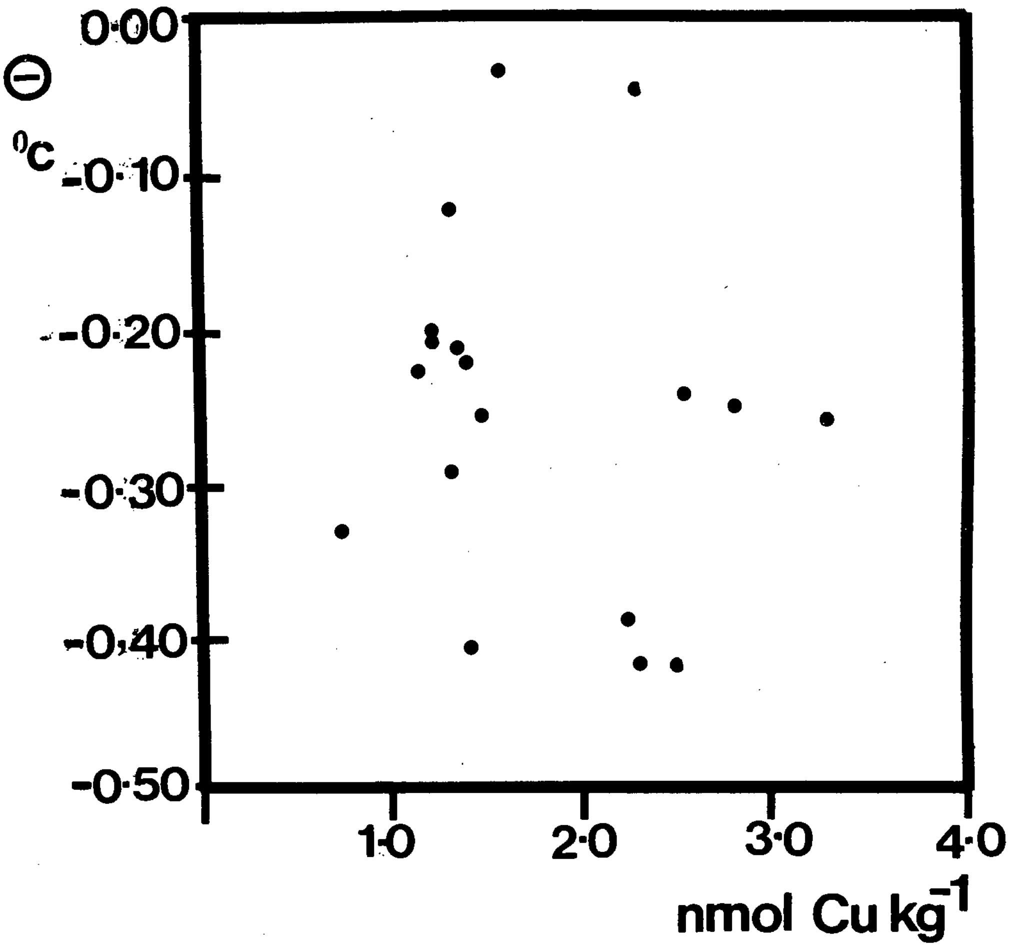
On the basis of the above results, some tentative conclusions can be made in conjunction with knowledge on other aspects of physical processes.

table 3.4

Copper-Silicate ratios for bottom waters in the Southern Ocean

Station	Depth (m)	Copper (nmol kg^{-1})	Silicate (µmol dm^{-3})	Cu/Si $\cdot 10^6$
1	2330	1.06	94.4	11.23
	2700	1.39	89.6	15.5
3	2700	1.23	100.1	12.3
	3150	0.73	95.0	7.7
7	3960	2.12	88.4	24
8	2700	2.80	112.5	24.9
	3600	3.25	113.5	28.6
9	3492	2.32	143.8	16.1
	4230	2.54	148.6	17.1

Fig. 3.3: A plot of potential temperature(0) against copper(Cu) to show the copper anomally developing in AABW in the Enderby basin.



In surface waters, the Cu/Si ratio should be regulated by the particular kind of primary producers characteristic of a given region (eg.diatoms and dinoflagellates).In Antarctic surface waters ,diatoms comprise the bulk of the primary producers but the surface water data gives little evidence of a constant Cu/Si ratio.(table 3.2) A chemical analysis carried out on planktonic species in Monterey bay area showed that the Cu/Si ratio also has a temporal variability(Martin and Knauer,1973). It appears therefore ,that the application of the Cu/Si ratio to surface waters presents some difficulty of interpretation. It is thought however,that if data were gathered spcifically for this purpose, the systematics of these variabilities would be better understood.

If there is indeed a flux out of sediments, the Cu/Si ratio for for interstitial waters requires that copper be enriched to a greater degree than silicate. The small number of samples collected at the depth range of AABW makes a definite conclusion difficult to attain. The data as given in Fig.3.3 show that copper input is in fact occurring. The scatter of points of the temperature-copper plot shows:

1. The coldest and hence 'new' AABW is lowest in copper content.

2. There are two groups of points; those lying towards the high copper concentrations are from waters thought to have flowed over the Weddell-Enderby basins.(AG 9)

This being so, the question is; can the progression of AABW and the silicate maximum anomaly(Edmond et al.,1979) be followed by an increase in the Cu/Si ratio? The change in magnitude of this ratio would be an indication of the source or sink role of the siliceous sediments in this region. From the data in table 3.4 ,the predicted result is that the Cu/Si ratio will increase progressively as the relative input of copper will exceed that of silicate.

The data shows that for some of the stations AG 3,4,5, the mean Cu/Si ratio for bottom water is $10\text{-}12 \times 10^{-6}$ but stations 7,8 show a ratio of 24×10^{-6}. At station AG 9 the ratio is 17×10^{-6}. On this basis it is proposed that the large Cu/Si ratios for the latter two groups are as a result of interstitial water flux and that the data of station 7,8 show a returning arm of the Weddell Gyre bottom water circulation after it has flowed over the Weddell-Enderby basin.

Though the ratio at AG 9 is somewhat different; it may simply be a result of a different interstitial water composition.

These findings give impetus towards further study of the boundary fluxes to and from abyssal sediments and bottom water. It is necessary to measure the bottom water gradients more precisely by closer spaced samples in conjunction with sediment cores at the same locality.

3.2 Zinc and Cadmium

Surface Waters

-14

The largest concentration gradient for both zinc and cadmium, is associated with the upper 400m of the water column (Fig.3.4;3.5).

As was discussed in section 3.1 , this gradient of an element with depth, is typical of chemical components that pass through the biogeochemical cycle in the euphotic zone.

The importance of faecal pellets on the vertical transport of cadmium is shown by the ratio below (Simpson,1981).

organisms: faecal pellets 1:5

water : faecal pellets $1:10^5$

This result clearly shows that biochemical and geochemical equilibria related to biomass production regulate the trace metal concentration in surface waters. The extent of this control is dependent on production rates which are relatively low in the Antarctic waters (El Sayed,1977).

Apparent correlations between trace metals and nutrients appear to confirm that biological mediation is an important factor in the overall balance (Bruland et al.,1978, Boyle et al.,1976) but that its effect is still too unpredictable. These corelations have been used as assessment tools on the reliability of trace metal data, this however assumes a model with global consistency a fact that is not observed.

From the surface water data there is little evidence that zinc and cadmium follow the nutrient systematics observed elsewhere (Bruland et al.,1978;Boyle et al.,1976) This could be a result of analytical differences but the low values and a consistent water column distribution indicates the data to be acceptable. For

Zinc and cadmium data from various point of the world oceans

Location	Position	Zinc nmol kg^{-1}	Cadmium nmol kg^{-1}	Reference
North East Pacific Ocean	36°N 123°W	0.13-1.16		Bruland et al.,1978
Indian Ocean	10°S 53°E	33.1	0.18	Danielsson,1
	19°N 56°E	10.8	0.19	" "
Sargasso Sea	33°N 56°W		0.27	Bender and Gagner,1976
North West Atlantic Ocean		17.1	0.32	Bewers et al.,1976
South Pacific Ocean	53°S 178°W		0.13	Boyle et al.,1976
Central Pacific Ocean	30°N 170°E		0.12	" " "
North Pacific Ocean	53°N 177°W		0.61	" " "
South West Antarctic Ocean	54°S 29°E	8.8	0.59	This Study
	51°S 32°E	9.7	0.79	" "
	49°S 35°E	5.3	0.52	" "

comparison, data from elsewhere appears on table 3.5. This can be seen on Fig. 3.4;3.5 where the vertical distribution of both zinc and cadmium shows a station to station consistency that is discussed in more detail below.

It is more likely therefore that good correlations are typical of regions of high productivity such as the North East Pacific (Bruland et al.,1978) where the vertical flux of zinc or cadmium exceeds the horizontal advection component in importance. Because production levels in this region are low, the vertical geochemical flux is not expected to have a major impact in the water column except in the immediate vicinity of the euphotic zone.

It was found that the ratio of trace metals with a suitable nutrient, eg:Cd/PO_4 , was a more useful parameter to study the distribution in the water column.

If the distribution and concentration of zinc and cadmium is in fact regulated by biochemical equilibria one would expect the ratios of Cd/PO_4 to hold in the organisms and the water column. Plankton analysis in the Sargasso Sea give the ratio as 6.5×10^{-4} (Boyle et al.,1976) and the local water column ratio as 3.5×10^{-4}. This result is in good agreement with the the result from this study,(3.8×10^{-4}) calculated as an average from the upper 100m(table 3.6).

The ratios do show spatial variability as shown by comparing,($Cd/PO4 = 1.8 \times 10^{-4}$) , in the South Pacific Ocean,(Boyle et al.,1976) , and the ratios obtained in this study(table 3.6). This variability could in part be ascribed to the finding that high activities of the PO4 anion selectively inhibit the uptake of

Nominal Latitude	Station	Zinc	Cadmium	Phosphate	Silicate	Cd/PO_4
		nmol kg^{-1}		$\mu mol\ dm^{-3}$		$.10^4$
67	5	15.3	1.10	2.14	70.1	5.1
67	6	17.3	1.09	2.21	70.6	4.9
54	9	11.6	0.59	2.33	57.7	2.5
51	10	9.2	0.79	2.12	21.3	3.7
49	11	6.3	0.52	1.81	12.1	2.9

mean $Cd/PO_4 = 3.8$

This data shows an interesting result in that although there is little latitudinal variation, the meridional or zonal variation is significant. The difference between the two legs could be important in view of their position straddling the Antarctic Divergence region.

The vertical profile for station AG 9 shows that the main zinc and cadmium gradients are associated with the pycnocline where an increase rate of accumulation is expected (Fig.3.4;3.5).

The subsurface gradient is especially noticeable in the case of zinc where at all 3 stations AG 9-11 (Fig.3.4) there is a definite enrichment by a factor of 2 to 3. The subsurface minimum is located well below the expected euphotic level, which may be attributed to the fact that the primary grazers, (copepods, euphausiids) prefer the more stratified layers near thef thermocline as opposed to the near isopycnal mixed layer.

The minimum at a depth of 100 m is also a feature of the cadmium profiles and some useful comparisons can be made between the profiles of AG 9 and AG 10 (Fig. 3.4).

1. The minima coincide with the same isopycnal surface = 27.20 although this is deeper towards the north.

2. In the case of zinc both minima lie in the vicinity of 7nmol kg .

On this basis it can be seen that the minimum structure has a large advective component (horizontal) thus both vertical fluxes and horizontal transport have to be taken into account to fully account for the gradient.

The zinc to cadmium ratio for the top 100m of the water column

Nominal latitude	Station	Zn/Cd	$\bar{X}$
68	1	6.6	
68	2	8.5	
68	3	9.2	
68	4	7.3	8.1
67	5	14.9	
67	6	13.9	
67	7	11.2	
67	8	13.2	13.6
54	9	14.5	
52	10	11.8	
49	11	10.8	

Table 3.8 Deep Water

Station	Depth	Zn [x]	Cd [x]	Zn/Cd
5	377	18.30	1.01	18.12
	568	14.82	0.82	18.05
	720	16.80	1.10	15.3
	960	16.0	1.10	14.6
	1150	15.0	1.01	14.9
	1445	17.10	1.19	14.4
	1933	14.9	1.01	14.8
	2700	16.60	1.28	13.0
	3420	16.50	0.82	20.1
9	720	11.20	1.24	9.03
	941	9.08	0.90	10.10
	1080	11.2	0.89	12.60
	1800	12.9	0.89	14.5
	2394	16.70	0.92	18.2
	3492	19.7	0.93	21.2
	4230	12.6	0.82	15.4
10	366	11.70	1.06	11.0
	900	12.10	0.78	15.5
	1311	10.30	0.76	13.6
	1803	13.30	0.81	16.4
	2883	15.0	1.03	14.6
11	348	18.00	1.00	18.0
	529	10.70	1.14	9.4
	720	8.92	1.13	7.9
	889	10.40	1.34	7.8
	1060	11.20	1.18	9.5
	2019	18.30	1.15	16.0
	2430	10.80	0.80	13.5

x nmol Kg^{-1}

The meridional surface water zinc and cadmium data (table 3.6),show that there is an enrichment southwards across the Antarctic Convergence . This trace metal meridional gradient correlates well with that observed for silicate and phosphate. It is likely that the southward enrichment is related to the upwelling of water that occurs as a result of the divergent wind stress curl in the Antarctic zone.

Deep Water

The deep water at all the stations shown on Figs.3.4;3.5 show little structure with respect to both cadmium or zinc. At all the stations the variabilty appears to be restricted to a mean point through the water column. This is further verified by the ratio of Zn/Cd which show minimal variability right to the bottom (table 3.8). This ratio holds at a mean of 15 with little change in AABW at AG 9 as opposed to that observed in the case of copper (section 3.2.2)

In contrast to copper, cadmium concentration in the interstitial waters show little enrichment relative to the water column which would mean a minimal flux into bottom water (table 3.2). The mean cadmium concentration is 13nmol kg^{-1} that would give an enrichment factor of up to 10 which as discussed previously results in an copper input into bottom water. This possibly accounts for the negligible impact of the interstitial water flux on the cadmium concentration in AABW.

4. METHODOLOGY

4.1 Sampling

It is generally recognized that the choice and process of sampling is the most critical step towards the acquisition of meaningful oceanographic data.(Orren,1979).

Though this view is not universal, (Bewers et al.,1981) advances in analytical procedures have in fact minimized sampling problems.

The greatest possible care was accordingly taken when sampling all the physicochemical parameters.

Temperature and Salinity

These were determined by a dual process:

1 - CTD (Neil Brown) continuous profiler sampling at a frequency of 30Hz

2 - 8 litre Niskin (PVC) bottles with reversing thermometers.

Unfortunately a technical malfunction with the electric cable of the CTD disabled the sensor and continuous profiling was abandoned. This data had to be gathered using reversing thermometers and discrete samples from selected depths. The obvious and unfortunate drawback was that no fine scale processes could be identified but the survey nature of the project also meant that continuous profiling was of secondary importance.

Oxygen

The CTD was fitted with an oxygen sensor which never performed to expected standards. The problem was linked to calibration of the sensor and its unpredictable response to sharp temperature gradients and pressure. The oxygen samples were also collected in B.O.D. bottles from the Niskin samplers and the oxygen imediately fixed (see analysis section) for onboard determination.

Nutrients

The nutrient samples were collected in 30ml polycarbonate vials and stored in a freezer (-15°C) for shore based analysis.

Trace Metals

The trace metals to be sampled for were Mn, Co, Ni, Cu, Zn, Cd and Pb. The sampling for the trace metals was potentially the most problematic and the time between collection of the sample, acidifying and subsequent freezing was minimized as far as possible.

Each sample was drawn into 1000ml medium density polyethylene bottles, acidified with 5.00ml of nitric acid (Aristar,BDH) from a Distrivar 5000 dispenser and frozen (-15°C) for shore based analysis.

The Niskin bottles used in this cruise were fitted with a silicone rubber closure to minimize contamination problems (Bewers and Windom 1982). A comprehensive exercise comparing a variety of sampling bottles and hydrowires has shown that modified Niskin bottles performed nearly as well as Teflon GO-FLO bottles (Bewers and Windom,1982). Their conclusion was that the unmodified GO-FLO and the Hydro-Bios samplers should be avoided and that a plastic coated hydro-wire should be used. The hydrowire used in the course of the project was a new stainless steel cable that at no point showed any sign of corrosion; hence problems of contamination should be small and in subsequent analysis no obvious contamination was noted.

4.2 Analysis

Salinity:

All salinity samples were analysed using a Plessey salinometer calibrated with IOS salinity standards. All values are expressed as per mil. as opposed to the new practical salinity scale (UNESCO 1980). The precision is estimated to be 0.005.

Oxygen:

The oxygen samples were prepared and analysed according to the Winkler titration method recommended by Strickland and Parsons (1975). All the analyses were carried out on board the vessel.

Nutrient Elements:

Silicate was determined by an in house modification (Mostert,1982) of a standard automated method (Folkard,1978). Phosphate was determined by the standard method recommended by Grasshoff,(1976), for the Autoanalyser.Nitrate was analysed by an automated method developed within the the Sea Fisheries Institute laboratory (Mostert,1982) whereby the nitrate was reduced to nitrite by passing through a reductor column packed with copper-coated cadmium granules buffered in an alkaline medium. Subsequently the nitrite is determined by the standard azo-dye synthesis method.

Trace Metals:

Before commencing analysis, a comprehensive review of the literature pertaining to the quantitative evaluation of trace metals from water was completed. The main problem associated with this kind of determination is that the levels are so low as to be beyond the direct detection limits of available instruments eg: Atomic Absorption Spectrophotometry(AAS)(Riley,1974). Thus,prior to analysis, the trace components have to be concentrated by one of two commonly used methods

1 - Solvent extraction

2 - Co-precipitation These methods have been extensively reviewed in the literature (Riley, 1975; Danielsson et al.,1978) and it is generally accepted that solvent extraction is rapid, precise and suitable for the analysis of

large numbers of samples. The co-precipitation method has serious drawbacks for subsequent AAS determination due to matrix problems (Danielsson et al.,1978).

More recently, methods have been developed to perform direct measurements on a sample, based on polarographic techniques (Lazar and Ben Yaakov 1980). The Anodic Stripping Voltammetry(ASV) methods have the advantage that they can be used to identify various species of a given element (Batley and Florence,1976;Batley and Gardner,1978). Comparative studies between AAS and ASV (Bewers et al.,1981) show that for most metals results are in good agreement but ASV requires great care in controlling experimental conditions. Neutron Activation Analysis (NAA), though a precise and accurate method, is no longer widely used due to its unsuitability in handling large numbers of small samples. The most common extraction procedure is one based on the extraction of metal-carbamate complexes from an aqueous to an organic phase (Riley,1975). Carbamates form inner sphere complexes with a variety of divalent metal ions and their low selectivity makes them suitable for multiple metal extraction. Most concentration procedures centre around this basic scheme, each having slight modifications in reagents and operation to suit the governing conditions.

4.3 Experimental

Apparatus:

Metal standards used were diluted from the Atomic Absorption Standards(BDH) of 1000ug ml^{-1}. The mixed standards were stored with concentrations at 100ug ml^{-1} and calibrated against laboratory standards made up by dissolving weighed amounts of each metal in (Aristar,BDH) nitric acid. The solvent used throughout was (BDH,Analar) chloroform; the ammonia solution was Analar,BDH grade and high purity nitric acid (Aristar,BDH) was used. All the water used was double distilled from quartz and the sea water for calibration purposes was collected well off shore on the Cape coast and filtered(0.45um) prior to use. The ammonium tetramethylene dithiocarbamate (APDC) (Spectrosol,BDH) was made up to 1% w/v strength in water to which 1ml of concentrated ammonia was added. This precaution avoided the formation of the insoluble protonated form of the chelator. No preliminary extraction or recrystallisation steps were necessary to purify the reagent. The second chelator 8-Hydroxyquinoline(oxine)(Analar,BDH) was made up to 1% w/v in chloroform.

Procedure details:

The extractions were carried out in 1000ml acid washed borosilicate glass separatory funnels with Teflon stopcocks and glass stoppers and the extracts were collected in acid washed 30ml glass vials. All glassware apparatus used in any way to handle reagents or samples was thoroughly washed with 10% v/v nitric acid and soaked for at least 24 hours in 5% nitric acid. Immediately prior to use, apparatus was rinsed with double distilled water. The determinations were done using a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer with a single slot air/acetylene burner for zinc and an HGA 500 furnace system for the remaining elements. All the lamps were of the Intensitron type and the system was optimized using standard solutions made up in both distilled and sea water.

The samples brought from the ship were kept frozen for up to 10 months while the necessary preparations were underway. It has been shown that acidified samples can be stored frozen for more than 2 years with no significant impact on the trace metal concentration (Marchant,1975)

Standards:

The method of standard additions was used to calibrate the instrument such that the range spanned the expected sample to sample variability. For each standard run there were 4 standards, 1 sea water blank and 1 double distilled water blank. Each sample had a nominal volume of 500ml and was weighed to determine the exact mass. The efficiency of standard recovery was always high and typically above 80%. An attempt was made to produce standards from artificial sea water but the results were disappointing and the method was abandoned.

Extraction:

In the extraction procedure decided on, a sample with nominal volume of 800ml was weighed out in the separatory funnel. The pH was adjusted to 5-6 using ammonia solution, 5ml of APDC were added and after a quick shake to mix this in, 10ml of 1% w/v oxine in chloroform were added. The extraction was carried out by vigorous shaking for a period of 60 seconds and the subsequent phase separation was complete after 10 minutes. The extract was run into a 30ml glass vial and 1ml Aristar nitric acid added. The complexing agents released the metal ions into the aqueous layer and wet ashing of the organic compounds was carried out by gentle warming to 150°C over a period of 6 hours. The resulting clear solution was dried at 150°C until a white ash remained in the vial. Care had to be exercised to stop the heating as soon as the ash was dry to avoid loss of the more volatile lead and cadmium. Wet ashing has been found to minimize loss of volatile components (Watling and Wardale,1977;Blanusa and Breski,1981). Initially, high blanks were obtained as a result of dust drawn into the fume cupboard with subsequent settling into the open vials. This was overcome by cutting a hole on the side of the fume cupboard and covering this with an air conditioning filter. The ashed residue was redissolved in 5.00ml 10% v/v Nitric acid and was then ready for determinations by AAS. The problem of pH control was studied and it was found that a slightly acidic solution(pH 5-6) gave the best precision. This pH avoided the loss of iron and manganese through hydrolysis, a phenomenon that has also been observed elsewhere (Danielsson et al.,1978). No buffer was used as it was found to have minimal effect on analysis and aggravated the contamination. Oxine was chosen since carbamate chelators having S functional groups favour complexing the more polarizing metals but do not complex as efficiently with the polyvalent species Fe III and Mn IV.

5. CONCLUSION

The main objective of this project was an attempt to understand the processes which affect the distribution of selected trace metals particularly, copper, zinc and cadmium, in the Southern Ocean south of South Africa. The results showed that the distribution of trace metals cannot be viewed in terms of a simple one dimensional input - output model since both physical and geochemical processes interact closely to regulate the observed distribution. Horizontal advection of water masses and, indirectly, input from the abyssal siliceous sediments were the most important processes affecting the distribution.

The physical data confirmed current ideas on the hydrodynamics of the Southern Ocean and were useful as a tool providing a framework for the interpretation of the trace metal distribution.

The following conclusions were established for the geochemistry of copper, zinc and cadmium:

1. Both zinc and cadmium showed a meridional enrichment in surface waters towards the south compared to sub tropical waters.

2. Copper showed a variability in the water column that could be related to a given stratum. Thus, it was found that Circumpolar Deep Water was relatively depleted in Cu (1.5-2.0 nmol) contrary to the expectation that copper follows nutrient systematics. This creates the potential of water mass typeing using their copper content provided the analytical accuracy and precision index is high

3. Even though the concentration ranges are within the accepted limits for oceanic waters, there is little indication of the metal systematics being the same as those of the nutrients. This may be a result of the low production levels in this region whereby the vertical biogenous particulate flux is of secondary importance.

4. The Cu/Si ratio was found to be a very useful parameter to infer the input of copper from interstitial water into bottom water. It was found that the siliceous sediments of the Enderby Basin are a source of Cu from the observed increase of the Cu/Si ratio with an increase in silicate content of Antarctic Bottom Water.

5. The vertical distribution of zinc and cadmium in deep water showed little variation, thus it is unlikely that the bottom sediments are a significant source of these elements. The upper part of the water column at the main subsurface metal gradient, showed that advection played an important role in determining the gradient and its depth. In view of this, the distribution of a given element cannot be viewed only in terms of a simple vertical one dimensional model.

It seems quite clear that even within the limited objectives of this project, it has been shown that trace metals can be used as tracers in the study of both physical and geochemical processes. Sampling and analysis have improved, and other determinations show an increased dynamic range as a result of better precision. The present dynamic range is still below the acceptable level of 10 but this can be improved by observing the following:

a- In view of the diversity of biogeochemical equilibria that affect the concentration and distribution of trace metals, future studies must be more specific (e.g. Sediment - Bottom water interface) to limit the number of variables and increase the sample density.

b- Trace metal work should be restricted to the study of one or two elements only by use of a highly selective chelating agent as opposed to present usage of non selective carbamate complexing molecules. The interpretation of the results obtained in the course of the project , have helped to focus future work on specific aspects of trace metal geochemistry in the Southern Ocean. On this basis, it is hoped that a more quantitative model can be set up to simulate the processes that regulate trace metal distribution.

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