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Summer-winter comparisons of oxygen, nutrients and carbonates in the polar seas*

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Abstract: Until very recently, marine chemistry studies in the polar seas were mainly performed in summer. Little or no chemical data were collected in winter because of operational problems. Yet, deep and bottom waters of the world oceans were mainly formed in winter in the polar regions. The lack of winter data in such regions has prevented scientists from accurately estimating the variation of chemical properties of deep and bottom waters as they move away from their formation regions.

Winter chemical data, including oxygen, nutrients, alkalinity, total CO_2, pH and P_{CO_2} have now been collected in the Weddell Sea, the South Indian Ocean, and the Bering Sea. The concentrations of certain chemicals, such as oxygen, were found to differ drastically from summer values. Some properties, such as alkalinity, on the other hand, do not show significant seasonal variations when compared at the same salinity and temperature.

1. Introduction

Subsurface waters are mainly formed in the high latitude oceans in the wintertime. One must therefore study the water chemistry in these regions in winter in order to understand the global biogeochemical cycle of chemicals. Owing to operational problems, however, few chemical measurements have been made in the high latitude regions in winter. For instance, we know of only seven oceanographic stations with high-precision carbonate data in the entire Indian Ocean south of 30°S. And all these stations were occupied in the austral summer (TAKAHASHI *et al.*, 1980). Not knowing the characteristic properties of the subsurface waters near their origin, and near the time of their formation, makes it difficult, if not impossible, to interpret variations in the carbonate chemistry in the Indian Ocean.

We recently had the opportunity to participate in winter cruises in the Weddell Sea, the South Indian Ocean, and in the Bering Sea. What follows will be the comparison between our winter data and the summer data collected by us and by other investigators.

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2. Study regions and measurements

a) SOMOV data: Concurrent pH and titration alkalinity (TA) were measured on the research/supply vessel, MIKHAIL SOMOV, of the Arctic-Antarctic Research Institute of Leningrad, USSR. The Weddell Polynya Expedition (WEPOLEX) started in Montevideo, Uruguay, on 9 October 1981, crossed the Polar Front, and entered the ice field at 5°E, 56°30′S. SOMOV reached its southernmost point within the ice field at 62°20′S, and left the ice edge at 57°30′S near the Greenwich Meridian after obtaining chemical data from 20 vertical stations. After crossing the Polar Front again, the ship returned to Montevideo on 25 November. The experimental technique and data are described and listed elsewhere (CHEN, 1982a; 1983; 1984). Supporting oxygen and nutrient data are described and listed in JENNINGS *et al.*, (1984), HUBER *et al.* (1983) and GORDON *et al.* (1984).

b) MARION DUFRESNE data: Concurrent pH, TA, total CO_2 (TCO_2) and nitrate (NO_3) data were obtained in the wintertime southwestern Indian Ocean as part of the INDIVAT 1 Expedition (INDIEN VALORISATION de

TRANSIT) aboard the French research/supply vessel MARION DUFRESNE. The ship departed La Reunion on 3 July 1984, reoccupied the GEOSECS station GS427, crossed the Subtropical Front at about 40°S, stopped in Crozet, reoccupied GS429 after crossing the Polar Front, then proceeded to Kerguelen and Amsterdam after crossing the Polar and Subtropical Fronts again, and returned to La Reunion on 4 August. Concurrent pH, TA and TCO_2 data were again obtained in the same general region in the austral summer of 1985 as part of the INDIGO 1/INDIVAT 3 Expedition (INDIGO stands for INDIEN GAS OCEAN) aboard the MARION DUFRESNE. The vessel departed La Reunion on 23 February and returned on 30 March after collecting chemical data from 23 stations including four GEOSECS stations (GS427–429, 454). The Subtropical Front was crossed at approximately 43°S and the Antarctic Front near 52°S.

The data description and listing are given in CHEN and POISSON (1986) and CHEN *et al.* (1986). The supporting oxygen and nutrient data are given in POISSON *et al.* (in preparation).

c) POLAR SEA data: The POLAR SEA left Dutch Harber, Alaska, on 18 February and returned on 19 March 1983, after moving in and out of the Bering Sea ice between 58° and 61°30′N and between 171° and 179°W. Concurrent pH, TA and oxygen concentrations were measured. The data have been described and listed in CHEN (1985) ahd CHEN *et al.* (1985).

Approximate study areas of these expeditions are shown in Fig. 1.

3. Comparison of the oxygen data

BROECKER *et al.* (1985) reported that the "surface ocean waters are almost always found to be supersaturated with dissolved oxygen," and that the amount of supersaturation averages about 7 μmol/kg or approximately 3%. The available data contradict this conclusion. Although BROECKER *et al.* (1985) investigated three of the largest data sets available (those of GEOSECS, NORPAX, and TTO), they did not examine the reports, including those containing winter data, published for high-latitude regions. LEVITUS (1982) summarized all data from the National Oceanographic Data Center as of 1978 and published the annual and seasonal mean oxygen saturation levels at the sea surface. The all-data annual mean indeed shows surface supersaturation except in upwelling areas of the eastern equatorial Pacific and the Southern Ocean. LEVITUS (1982), however, cautioned against a hastened conclusion, because the all-data annual mean may represent data from only one season, most likely summer. The Southern Ocean annual mean, for example, was shown to be a few percent undersaturated, but at that time sufficient winter data were not available. The recent winter data, to be discussed later, indicate an even lower degree of saturation. The then available and recent winter data also

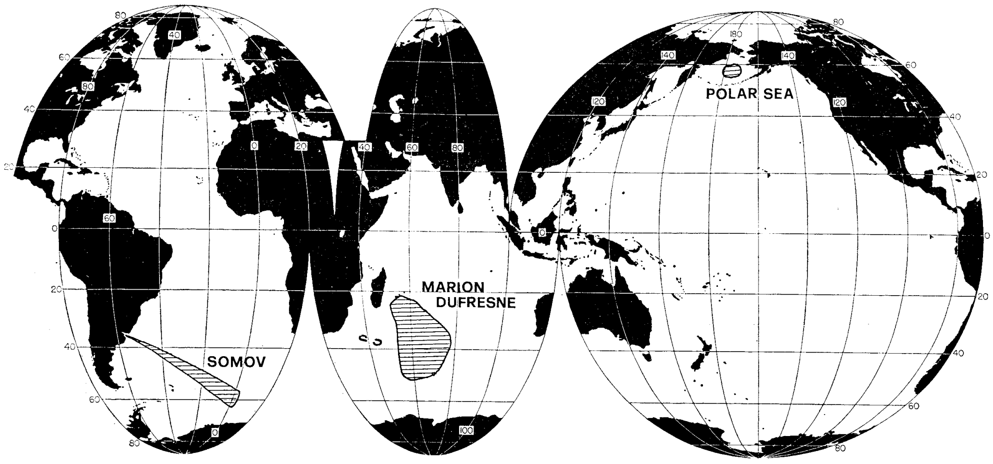

Fig. 1. Study regions of SOMOV, MARION DUFRESNE and POLAR SEA. Map provided by A. Mantyla.

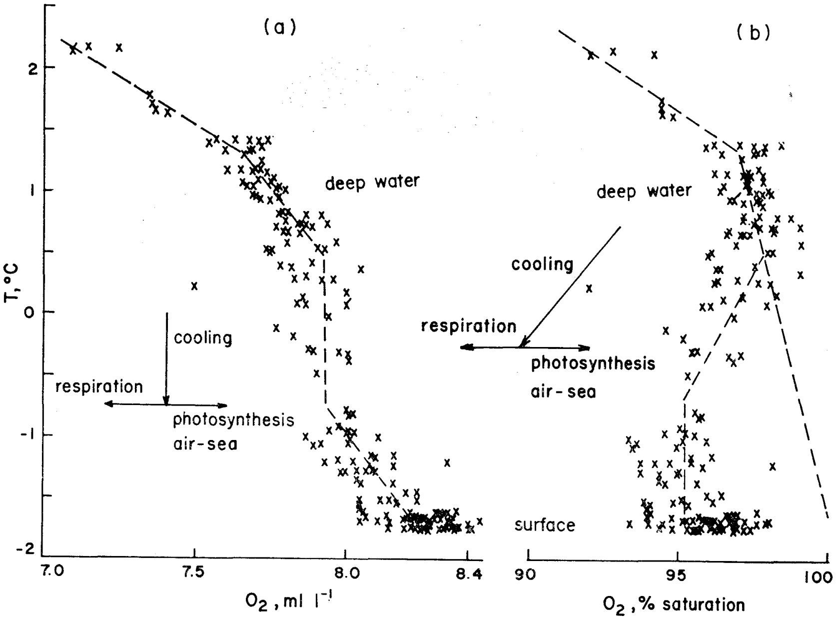

Fig. 2. Correlation between (a) temperature and oxygen, and (b) temperature and % oxygen saturation for Bering Sea shelf waters in winter (Taken from CHEN, 1985).

show undersaturation in the Bering Sea and the northern North Atlantic, but because the more abundant summer data show supersaturation, the annual all-data mean also shows supersaturation.

Clearly, not all surface ocean waters are supersaturated with oxygen, and certainly they are not always supersaturated. Analysis of oxygen saturation for the four seasonal periods is desirable, but we will only attempt to make the summer - winter comparison because of the limitation in data coverage.

As early as 1963, SMETANIN (1963) reported that wintertime northeast Pacific surface water is slightly undersaturated with oxygen.

IVANENKOV (1964) reported that nealy all of the Bering Sea in winter absorbs oxygen. He reported an average of 6% undersaturation in the western Bering Sea, a value later confirmed by REID (1973). A similar degree of oxygen undersaturation exists in the northwestern North Pacific Ocean in winter (HAKODATE MARINE OBSEVATORY, 1967; REID, 1973; 1982). The wintertime northern Gulf of Alaska surface water data and our POLAR SEA data on the eastern Bering Sea shelf also show systematic undersaturation in winter (SIO Reference 70-5, 1970; CHEN, 1985; CHEN *et al.*, 1985). The oxygen content of the POLAR SEA winter surface layer is higher than that of the deep layer on the ice-covered shelf (Fig. 2a), but the degree of saturation (CHEN, 1981) is reversed, *i. e.* most of the deep shelf water is more highly saturated than that of the surface water (Fig. 2b). This phenomenon is not observed in summer when both the oxygen content and the degree of saturation of the surface water are higher than those of the deep shelf water (*e. g.* HATTORI, 1977; 1979).

In summer, shelf oxygen data show extreme variability, governed by biological processes (CODISPOTI *et al.*, 1986). Winter oxygen, however, seems to mix conservatively regionally as suggested by segments of linear temperature vs oxygen correlations (Fig. 2a), discussed in detail in CHEN (1985).

Waters cooler than -0.6°C are all in the homogeneous surface layer and have higher oxygen concentration at lower temperature (Fig. 2a). All waters below -0.6°C, however, remain at about 5% undersaturation (Fig. 2b), suggesting that air-sea exchange and photo-

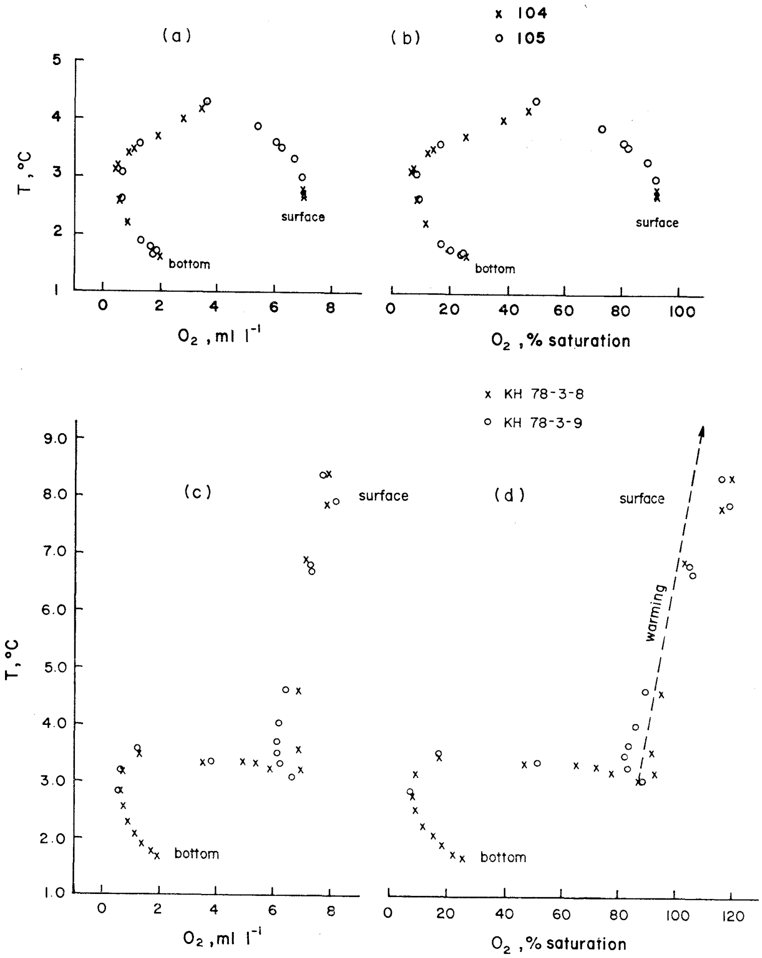

Fig. 3. Correlation between (a) temperature and oxygen, (b) temperature and % oxygen saturation of our winter Aleutian Basin data, and correlation between (c) temperature and oxygen, (d) temperature and % oxygen saturation of the summer *Hakuho Maru* data from the same location. The broken line shows the theoretical slope (Taken from CHEN, 1985).

synthesis cannot replenish oxygen fast eoungh to compensate for upwelling of water with lower O_2 content, respiration, and cooling effects. The result is that the surface waters actually show a lower degree of oxygen saturation than most deep waters (CHEN, 1985; CHEN *et al.*, 1985).

Deep waters for POLAR SEA stations (104 and 105) in the Aleutian Basin show a minimum in oxygen (Fig. 3a). The homogeneous, ice-free surface layer is also undersaturated with respect to oxygen by about 8% (Fig. 3b). The winter surface water oxygen concentration is similar to the value found in the minimum temperature layer in the summer. Summer data from the same locality (stations KH78-3-8 and KH78-3-9 of the *Hakuho Maru* Cruise; HATTORI, 1979) are plotted in Fig. 3c and 3d for comparison. Seemingly, summer warming raises the temperature, but the oxygen content of the surface layer does not increase by much except in the top thirty meters, where supersaturation is obviously caused by enhanced photosynthesis. In winter, enhanced vertical mixing and rapid cooling, unmatched by slower air-sea oxygen exchange and photosynthesis, produce undersaturation in the surface layer (IVANENKOV, 1964; REID, 1973; CHEN, 1985). BRUJEWIEZ *et al.* (1960) also found an undersaturation as much as 20% in the summer minimum-temperature layer in the Sea of Okhotsk, with the lowest degree of saturation on the continental shelf off Siberia and Sakhalin Island where intensive cooling occurs in winter.

The situation is similar in the Weddell Sea, based on the comparison of the SOMOV (CHEN, 1982a; 1984; HUBER, *et al.*, 1983; GORDON, *et al.*, 1984), GEOSECS (TAKAHASHI *et al.*, 1980) and other data in the literature (BRENNECKE, 1921; DEACON, 1940; OB, 1958; 1959; SECRETARIA DE MARINA, 1959a, b, c; IGY, 1961; some of these data need to be adjusted due to systematic analytical error). An ice-free summertime GEOSECS Atlantic station, GS89, is located at 0.0°E, 60.0°S which is very close to the ice-covered SOMOV station 33 (0°20′E, 60°S). The Θ/S plot for waters below the Θ_{min} layer at GS 89 is essentially the same as the plot at SOMOV 33. The Θ/AOU plot (Fig. 4) below the Θ_{min} layer at GS89 is also similar to the plot at SOMOV 33. The SOMOV 33 data show a high AOU (apparent oxygen utilization) value of 50 μmol/kg at the surface because the surface water is mixed with low-oxygen Weddell Deep Water, while the ice blocked the input of atmospheric oxygen (GORDON *et al.*, 1984). This finding supports the suggestion of WEISS *et al.* (1979), EDMOND *et al.* (1979), MINAS (1980), LYAKHIN and RUSANOV (1980) and CHEN (1982b) but disagrees with the Arctic work of GOSINK *et al.* (1976) and F. HERR (private communication, 1983) who found that the annual Arctic sea ice is permeable to gases.

Our winter data in the Bering Sea also suggest some air-sea exchange, but the exchange could have happened in the numerous leads and polynyi that we encountered in the Bering Sea but not in the Weddel Sea. Furthermore, unlike the annual Arctic sea ice which has many brine channels, the Weddell Sea ice has a large content of frazil ice with few brine channels, resulting in low permeability (ACKLEY *et al.*, 1980; 1982; CLARKE and ACKLEY, 1982). The late-winter, early-spring Weddel Sea surface water is at about 86% saturation, higher than the 60% for deep waters (BRENNECKE, 1921; GORDON *et al.*, 1984). The winter SEAMUNDSSON and HUDSON data (MALMBERG, 1983; CSS HUDSON, 1984) in the northern North Atlantic Ocean also show systematic oxygen undersaturation (as low as 10% undersaturation) within or out of the ice field.

The above discussion clearly indicates that the high-latitude regions are probably undersaturated

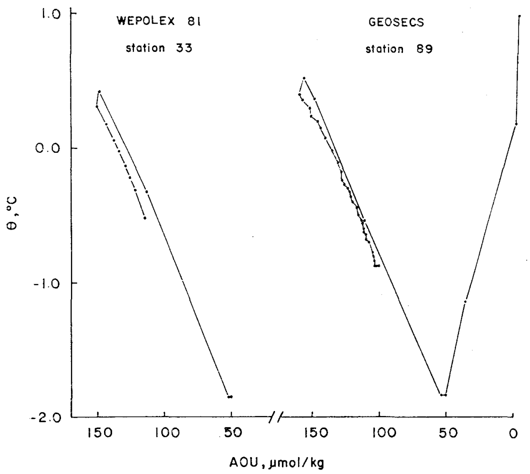

Fig. 4. Θ/AOU plot for WEPOLEX station 33 and GEOSECS station 89 in the Weddell Sea. The temperature minimum layer for the GEOSECS data is at about −1.8°C.

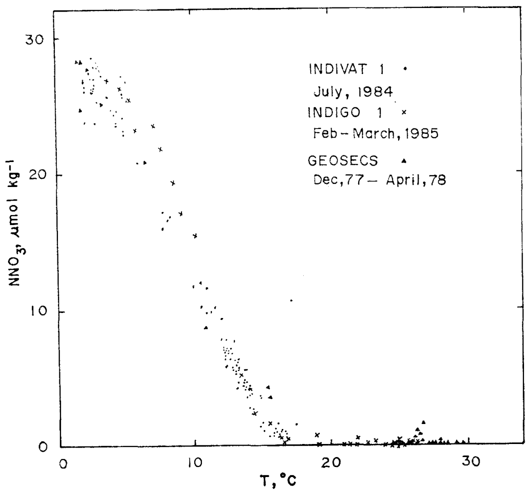

Fig. 5. Surface normalized nitrate concentrations vs temperature for the GEOSECS, INDIVAT 1 and INDIGO 1/INDIVAT 3 data in the south Indian Ocean.

with oxygen in winter, although water chemistry beneath the ice varies from place to place, and we cannot yet generalize the findings in one area to represent other regions. As further note, ANDERSON and DYRSSEN (1980) reported surface oxygen supersaturation within the summer Barents Sea ice field, which is, no doubt, due to photosynthesis.

4. Comparison of the nutrient data

Surface nutrient values frequently show significant variations between cruises even when data from the same location are compared. For instance, at GS 429 occupied in summer (Feb. 1978), the surface nitrate concentration was 20.2 μmol/kg (WEISS *et al.*, 1983). The INDIGO 1/INDIVAT 3 value was 21.2 μmol/kg (March 1985) and the INDIVAT 1 value was 24.5 μmol/kg (July 1984). For unknown reasons, however, the surface nitrate value correlates linearly with temperature when the nitrate concentrations are normalized to a constant salinity basis. The normalized nitrate ($NNO_3=NO_3\times35/S$) data from the above three cruises are shown in Fig. 5. These three temperature trends show much smaller variations. Phosphate and silicate behave in a similar way. Parts of the natural variations, such as those due to evaporation and precipitation, are removed by normalization, thus the resulting trends reflect mainly biological and mixing processes.

5. Comparison of the alkalinity and total CO_2 data

The surface alkalinity and total CO_2 values show large seasonal variations when compared in the same region, even when the effect of precipitation and evaporation is considered. The potential temperatue is plotted against normalized total CO_2 ($NTCO_2$) for the WEPOLEX and GEOSECS data in the Weddell Sea (Fig. 6). The WEPOLEX winter data agree with the GEOSECS summer data below the temperature minimum layer, which is the remnant winter surface water (CHEN, 1984; POISSON and CHEN, 1987). The summer surface water, however, is lower by as much as 50 μmol/kg in $NTCO_2$ because of biological consumption. The NTA values are approximately 10 μeq/kg lower.

The surface NTA and $NTCO_2$ values, how-

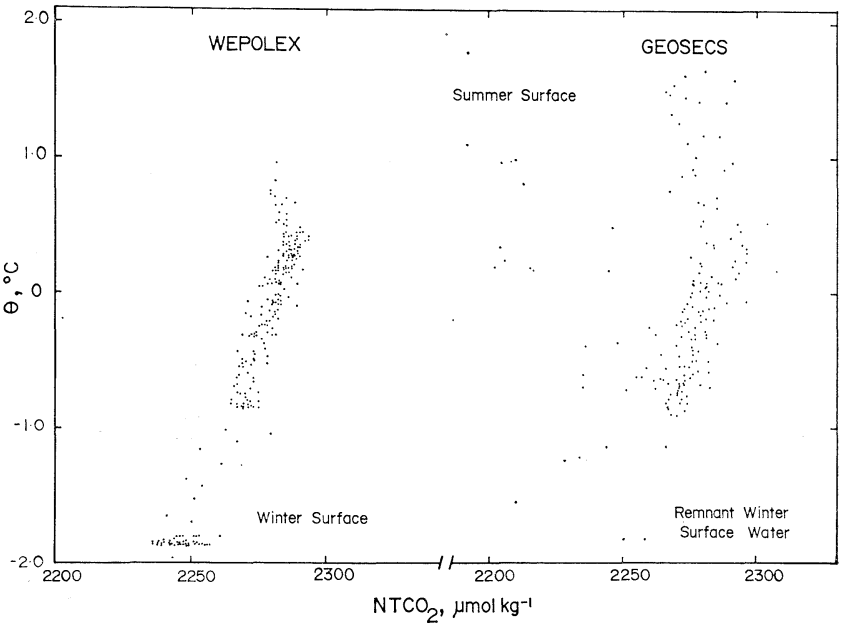

Fig. 6. Potential temperature vs normalized total CO_2 for the WEPOLEX (all data) and GEOSECS (stations 79, 82, 85, 87 and 89) expeditions in the Weddell Sea. The temperature minimum layer for the GEOSECS data is between 0 and -1.8°C where $NTCO_2$ approximately 2,250 μmol kg^{-1}.

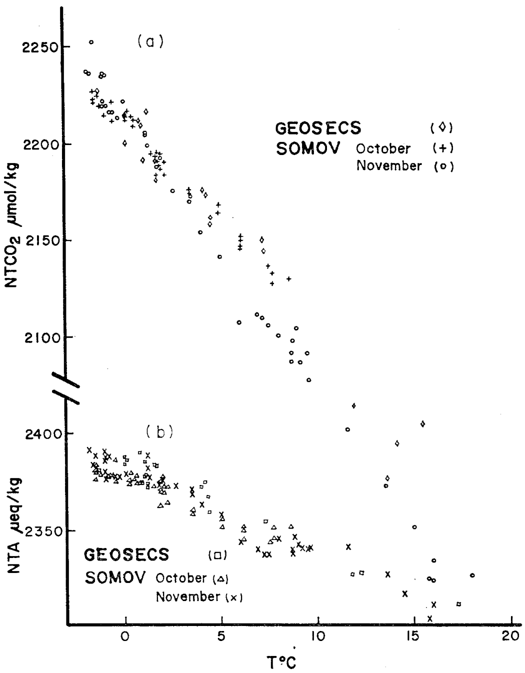

Fig. 7. Surface (a) normalized total CO_2 and (b) alkalinity vs temperature for the GEOSECS and SOMOV data in the south Atlantic Ocean.

ever, show less seasonal variation when compared at the same temperature. The normalized surface alkalinity and total CO_2 seem to decrease steadily with increasing temperature (CHEN and MILLERO, 1979; CHEN and PYTKOWICZ, 1979). The GEOSECS $NTCO_2$ data (Dec. 1972 - Jan. 1973) in the southern South Atlantic Ocean are higher than the October SOMOV data by 6 μmol/kg and are significantly higher than the November SOMOV data above 5°C (Fig. 7a). These differences reflect a possible seasonal effect due to changes in biological productivity. The biological productivity, however, does not significantly affect alkalinity. Indeed we could not detect any seasonal variability in NTA vs temperature correlations among the GEOSECS, SOMOV October and SOMOV November data (Fig. 7b). The GEOSECS NTA data are approximately 5 μeq/kg higher than the SOMOV data, but the difference is slightly smaller than the combined experimental error.

Data in the south Indian Ocean also show strong seasonal variations in $NTCO_2$ when the GEOSECS data are compared with the INDIVAT 1 and INDIGO 1/INDIVAT 3 data. The difference in NTA is smaller, on the order of 10 μeq/kg, only slightly larger than the combined analytical error.

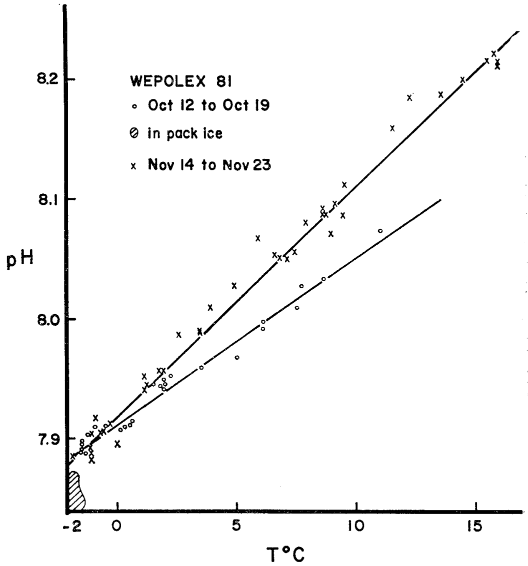

Fig. 8. Surface pH values (measured at 25°C) vs temperature of the SOMOV data (taken from CHEN, 1984) in the South Atlantic Ocean.

6. Comparison of the pH and P_{CO_2} data

The surface pH values (measured at 25°C) also correlate linearly with temperature, and seasonal variations are evident from the SOMOV data (Fig. 8). MARION DUFRESNE data in the south Indian Ocean also show linear correlations with temperature but there the summer trend does not differ significantly from the winter trend below 18°C.

It is well known that pH variations in the subsurface waters follow variations in oxygen. Fig. 9 shows the pH vs temperature correlations of our POLAR SEA winter and *Hakuho Maru*'s 78-3 summer Aleutian Basin stations (HATTORI, 1979). The curves are of similar shape as the temperature vs oxygen plots (Figs. 3a, c). Our deep water values are systematically higher than the *Hakuho Maru* data by 0.05 pH units, probably owing partly to a difference in calibration. The winter surface value would agree with the summer value at the minimum temperature layer if the summer value is systematically shifted up 0.05 units. The summer surface pH value are

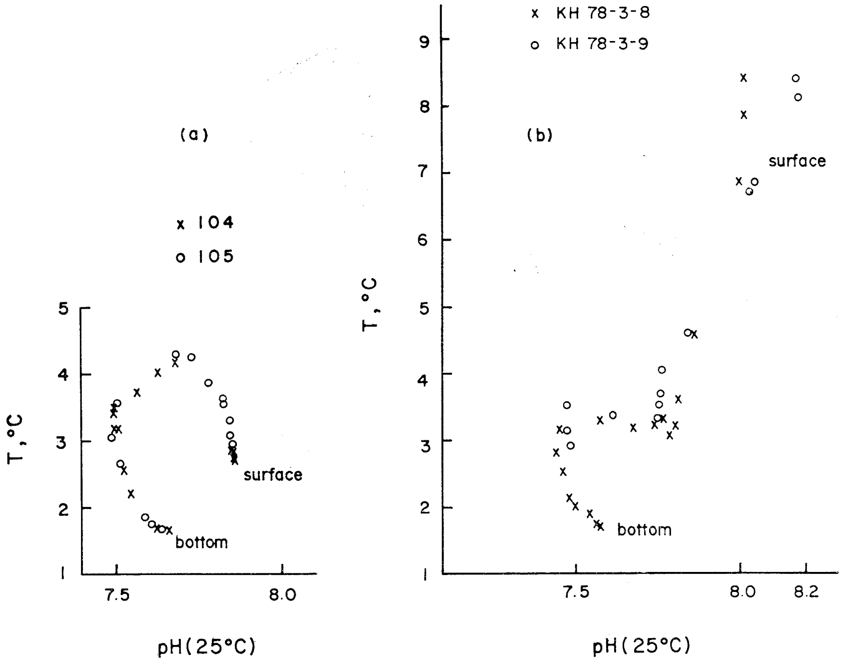

Fig. 9. Correlation between temperature and pH values (measured at 25°C) of (a) our winter Aleutian Basin data and (b) the summer *Hakuho Maru* data from the same location (Taken from CHEN, 1985).

significantly higher than the winter value, reflecting CO_2 consumption by primary productivity (CHEN, 1985).

P_{CO_2} values are also known to show large seasonal variations (DEACON, 1940). Strangely, our SOMOV data (CHEN, 1984) and the data of TAKAHASHI (private communication, 1982) and TAKAHASHI and CHIPMAN (1982) are similar to the GEOSECS data (TAKAHASHI *et al.*, 1980) near 60°S in the south Atlantic and are nearly in equilibrium with the atmosphere. Rapid cooling of the surface water in winter reduces P_{CO_2}, but upwelling and entrainment (GORDEN *et al*, 1984) increase P_{CO_2}. It is fortuitous that the net result is near equilibrium with the atmosphere. These observations prompted the suggestion that the Antarctic surface waters are likely to be in equilibrium with the atmosphere throughout the year (CHEN, 1984; TAKAHASHI, private communication, 1982; TAKAHASHI and CHIPMAN, 1982). Recent observations of TAKAHASHI (private communication, 1985), however, do show large temporal variations in the Southern Ocean. Fig. 10, based on the SOMOV data,

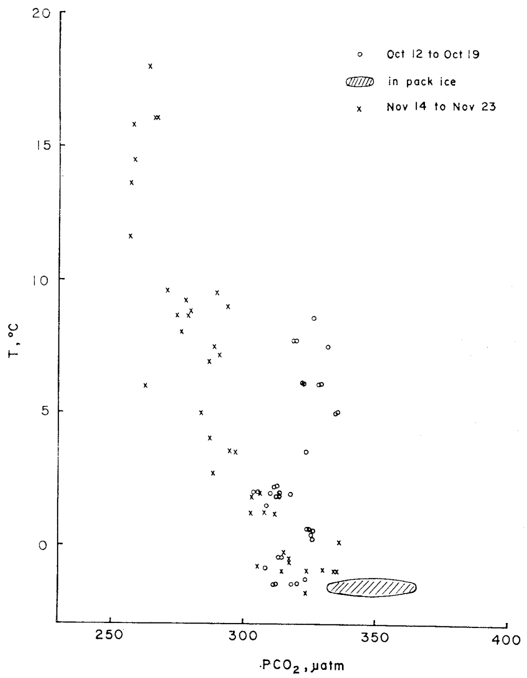

Fig. 10. Surface P_{CO_2} values vs seawater temperature of the SOMOV data (taken from CHEN, 1984) in the south Atlantic Ocean.

also shows large October to November changes in PCO_2 at high temperatures.

7. Conclusion

Certain chemical properties such as oxygen, pH and PCO_2 show large seasonal variations in the polar seas. Nutrients, alkalinity, and total CO_2 also vary significantly at the same location. But the variation is much reduced when compared at the same salinity and temperature. The seasonal variability in the normalized alkalinity is not much higher than the analytical error.

We believe that winter values should be used in preference to the summer values when one needs to know the initial, or preformed, concentrations of chemicals for deep and bottom waters. Without such information, calculations of production or consumption rates of chemicals are frequently subject to large error.

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極海中の酸素，栄養塩，炭酸塩の夏季と冬季の比較

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要旨: 極海における海洋化学的調査は，ごく最近まで主として夏季に行われてきた。作業の困難さもあって，冬季の化学的データはほとんど得られていなかったが，世界の海洋の深層底層水は極域で冬季に形成されるから，極域における冬季のデータの欠如は深層底層水が形成された場所から移動していくにつれてその化学的特性がどのように変化するかを厳密に推定することを困難にしていた。現在では，冬季のウェッデル海，南インド洋，ベーリング海において酸素，栄養塩，アルカリ度，全炭酸，pH，$P\mathrm{CO_2}$ などのデータが得られている。これらを夏季のデータと比較してみると，酸素などではその濃度に顕著な差異があるのに対して，アルカリ度などでは同一塩分・同一水温で比較しても顕著な季節変化は認められないことがわかる。