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Distribution of carbon dioxide partial pressure in surface waters of the Southwest Indian Ocean

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ABSTRACT

Using data from different seasons (July 1984 and February–March 1985), we describe the geographical, annual, and seasonal variability of the partial pressure of carbon dioxide (pCO_2) in sea surface waters of the Southwest Indian Ocean. In Subtropical regions, we observed pCO_2 values almost 45 μatm higher in summer than in winter. This variation is produced principally by the seasonal change of sea surface water temperature. In contrast, in the Subantarctic region, pCO_2 values 25 μatm lower in summer than in winter in response to the predominant seasonal biological activity were observed. This characteristic phase change of the seasonal oceanic surface pCO_2 signal with latitude appears to be a global phenomenon and is mirrored in the northern hemisphere. A comparison with GEOSECS data shows good agreement between our total CO_2 profiles and the earlier observations. In the southern region of the Antarctic convergence, both the measured and calculated pCO_2 values agree with those of the GEOSECS program, and confirm that this region of the ocean is probably a source of CO_2 to the atmosphere throughout the year.

1. Introduction

One of the most important societal problems that will confront us in the next few decades will be the increase in atmospheric temperature and related effects resulting mainly from the fossil fuel induced increase in atmospheric carbon dioxide concentration. Many studies are presently underway to document this process, and to predict its future course.

A model developed by Pearman et al., (1983) shows that a large amount of CO_2 from fossil fuel combustion processes is taken up by the ocean, especially in high latitudes. This model also indicates that the amount of CO_2 penetrating the ocean has increased by a factor of two during the last forty years. Though many estimations of the carbon cycle parameters have been reported (Salomon at al., 1985), CO_2 exchanges across the air-sea interface need to be measured with greater accuracy in order to quantify the efficiency of the ocean to CO_2 absorption.

On a global scale, one would expect an increase of CO_2 penetration in seawater when moving from the equator towards the poles (Wattenberg, 1933; Takahashi, 1961; Keeling, 1968; Takahashi et al., 1980a; Sundquist and Plummer, 1981); this is globally shown in the model calculation of Pearman et al., (1983). The geographical variation of CO_2 penetration in the ocean is mainly due to the increase of CO_2 solubility with decreasing temperature (Weiss, 1974) and to the advection of surface water into the deep ocean. The CO_2 penetration into the deep ocean is usually produced by three mechanisms: convection in region where deep water is being formed, diffusion through the thermocline, and sinking of particulate matter. The relative contribution of these processes, however, is still difficult to quantify.

Only two relatively small areas on the ocean

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surface are at the origin of deep waters; in the North Atlantic Ocean and in the Antarctic Ocean in the Weddell sea and along the Antarctic continent (Tchernia, 1980; Broecker and Peng, 1982). Recent studies suggest that CO_2 penetration in the North Atlantic Ocean, as well as in high latitudes in the Southern Ocean, is quite small (Brewer, 1978; Minas, 1979; Weiss et al., 1979; Chen, 1982; Brewer et al., 1989; Tans et al., 1990). For example, the Weddell Sea, an active zone of deep water formation, does not seem to be a strong sink for CO_2 (Poisson and Chen, 1982 and 1987). On the other hand, north of the antarctic convergence, the observed low pCO_2 values suggest that very strong CO_2 penetration occurs there. Thus, the subantarctic zone is possibly one of the most important regional oceanic sink for atmospheric CO_2.

Unfortunately, the Southern Ocean is particulary poorly documented with regard to the details of the CO_2/carbonate system. The reason for this poor description is not the lack of interest but mainly the lack of winter data and paucity of accurate summer CO_2 data for this region.

In this paper, we present a first study of the oceanic CO_2/carbonate system focused on the variations of pCO_2 in the upper layer of the southwest Indian Ocean during July 1984 and March 1985.

2. Location of the samples

All the samples were collected during two cruises aboard the R/V MARION DUFRESNE in the southwest Indian Ocean from latitude 23°S to 53°S and from longitude 50°E to 76°E. The tracks of the cruises and stations location are shown in Fig. 1.

The first cruise (INDIVAT I) was performed in July 1984 during the austral winter; it departed from Réunion Island, went by Crozet, Kerguelen and Nouvelle Amsterdam islands, and returned to Réunion Island. Sea surface water samples were collected at 1-h intervals when the ship was underway. This was done using a sea water intake located at the bow about 4 m below the surface. Temperature and salinity were recorded during the entire cruise at the intake by a thermosalinograph and measurements of pCO_2, total alkalinity (TA), total inorganic carbon (TCO_2), salinity and oxygen were performed directly on board. Deep samples were also collected at two hydrographic stations using a CTD-Rosette system. These stations, at positions 27°S 57°E and 47°40′S 57°50′E, match the G427 and G429 stations of the GEOSECS program, respectively. The corresponding data from the GEOSECS program provides us with a data set with which to compare

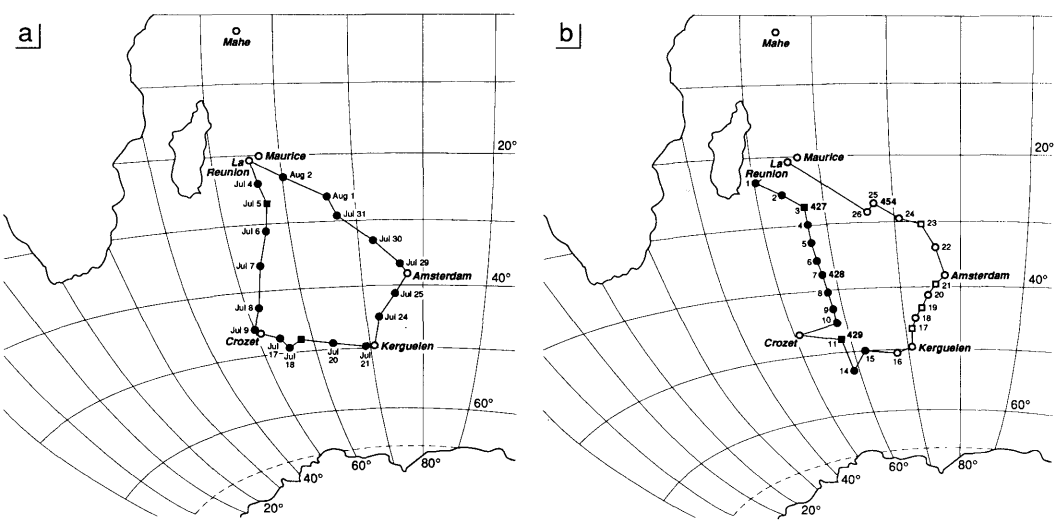

Fig. 1. Station location and tracks of the cruises (a) July 1984; (b) February–March 1985.

our results, in order to investigate the seasonal and interannual evolution of these waters.

The second cruise (INDIVAT III) was performed during the southern summer. The R/V MARION DUFRESNE departed from Réunion Island on 23 February and returned on 30 March 1985 (Fig. 1). At each of the 23 hydrographic stations between 23°S and 53°S, samples of seawater were collected at 36 different depths from the surface to the sea floor using a CTD-Rosette system. Stations 3, 7, 11 and 25 match with the G427, G428, G429 and G454 stations of the GEOSECS program, respectively. Several physical and chemical parameters were measured at each depth (Poisson et al., 1988); only the parameters of the surface CO_2/carbonate system will be discussed here. Sea surface samples were also collected between Nouvelle Amsterdam and Réunion islands. The following parameters: TA, TCO_2, pCO_2, pH, oxygen, nutrients, and salinity were measured on these samples. Temperature and salinity were recorded as during the INDIVAT I cruise.

3. Experimental

Analytical techniques used to measure each parameter have already been described in detail in Poisson et al., (1988). For the sake of clarity, we present here a brief reminder of the analytical techniques used in the determination of TA, TCO_2 and pCO_2.

3.1. Total alkalinity and total inorganic carbon measurements

A potentiometric method derived from the one first described by Dyrssen (1965) and by Dyrssen and Sillén (1967), and modified by Bradshaw et al., (1981) was used to determine both TA and TCO_2. These latter were computed from the raw data using the Gran (1952) method, and the polynomials of the apparent dissociation constants of carbonic acid computed by Dickson and Millero (1987) and recommanded by the Joint Panel on Oceanographic Tables and Standards (UNESCO, 1987). To avoid CO_2 exchanges with atmosphere, titrations were performed in a closed cell. In order to keep the ionic strength of the sample approximately constant during the course of a titration, the ionic strength of the acid (HCl 0.1N, PROLABO Normadose) was adjusted to 0.7 N with NaCl. We used solutions of Na_2CO_3 with the same ionic strength as primary standards (Goyet et al., 1985). Water circulating around the cell maintained the sample at a constant temperature, to within 0.1°C. Measurements were carried out on board within 24 h following the sampling. The precision of the method was better than 0.2% for TA (± 3 ueq kg^{-1}) and 0.3% for TCO_2 (± 6 μmol kg^{-1}).

During March 1985, duplicate samples were collected in order to measure TCO_2 by two methods; potentiometric titration on board by us and the manometric technique on shore at SIO by C. Keeling. The results, described along with the rest of the data from this cruise (Poisson et al., 1988), show a mean difference of 6 μmol kg^{-1} for the sea surface waters, with corresponds to a difference of almost 12 μatm in pCO_2. This disagreement is smaller than in the North Atlantic ocean, but is still significant.

3.2. Partial pressure of carbon dioxide

Oceanic and atmospheric pCO_2 was measured by gas chromatography. The measuring system derived originally from Weiss (1981), consisted of a gas chromatograph DELSI, IGC 122, an equilibrium cell and a microcomputer Commodore, CBM 4032 (Beauverger and Lemarchand, 1988). The cell 250 ml plexiglass cell was filled with the seawater sample and closed after overflowing. A standard gas (Air Liquide, 350 μatm CO_2 in air) was used to flush all the tubes joining the cell to the gas chromatograph, before filling the headspace (approximately 15 ml) surmounting the water sample. The headspace was created by a piston connected to the cell. Fig. 2 shows a simplified diagram of the equilibration cell. Measurements were conducted in wet air at atmospheric pressure and the temperature was maintained constant by water circulating around the cell. Standard gas and seawater samples were equilibrated for 5 min, both by magnetic stirring and gas phase bubbling in the liquid phase. The aliquot of the gas phase contained in the calibrated loop was then injected into the gas chromatograph. The CO_2 gas was separated by a column of porapack S and reduced to methane using a nickel catalytic column at 400°C before being analysed by a flame ionisation detector (FID). Each measurement in atmospheric

air or in seawater was flanked with a couple of appropriated standard gas (Air Liquide, 251, 320, 380 and 450 $\pm$ 0.25 μatm CO_2 in air). Temperature corrections on seawater samples were calculated with the polynomial developed by Copin-Montegut, (1988). The pCO_2 results are given at the local atmospheric pressure in wet air. The precision was estimated to be better than 0.8% for atmospheric pCO_2 and 1% for seawater pCO_2 values.

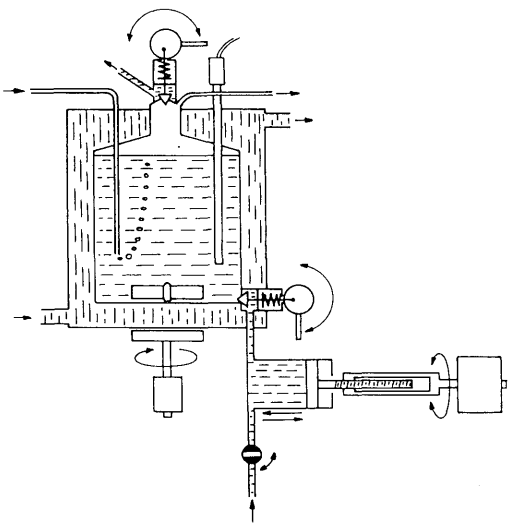

Fig. 2. Simplified diagram of the equilibration cell for pCO_2 measurement.

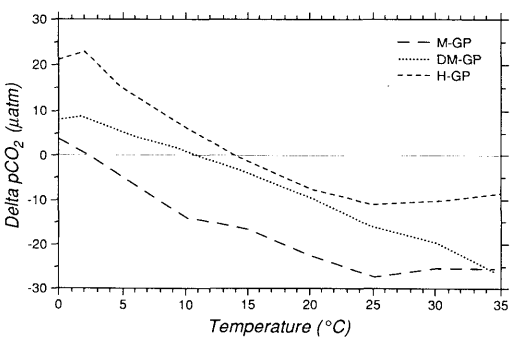

Fig. 3. Differences between computed pCO_2, using a property pair TA-TCO_2 and the dissociation constants of carbonic acid from Goyet and Poisson (GP), Hansson (H), Mehrbach et al. (M), and Dickson and Millero (DM).

3.3. Calculation of pCO_2 from TA and TCO_2 data

PCO_2 in seawater was also calculated from measured TA and TCO_2 values using the algorithms developed for the GEOSECS program (Takahashi et al., 1980b). The apparent dissociation constants of carbonic acid used are those recommended by the JPOTS (UNESCO, 1987).

The discrepancies which exist between the measured and calculated pCO_2 values are not yet well explained; they are mainly attributed to the two apparent dissociation constants of carbonic acid in sea water medium (UNESCO, 1987). Recently, a careful determination of these constants has been performed by Goyet and Poisson (1989). Fig. 3 illustrates the difference between computed pCO_2 using this new data set and those of Mehrbach et al. (1973), those of Hansson (1973) and those recommended by the UNESCO report (1987). Although these differences can reach almost 30 μatm, the constants alone cannot be responsable for the observed differences between measured and computed pCO_2. For instance for these cruises in the southwest Indian ocean, the difference observed between measured and calculated pCO_2 varied at random from 2 μatm to 25 μatm.

4. Position of the fronts

The Southern Ocean is characterized by a system of fronts which separate different water masses. The geographical position of these fronts, which are difficult to locate by surface parameters alone, shows significant annual and seasonal variability. For instance, south of Africa, over a period of 25 years, for the same longitude, the latitudinal position varies 4° for the Subtropical Convergence (STC), 3.5° for the Subantarctic Convergence (SAC) and 5° for the Antarctic Polar Front (APF). Furthermore the width of the fronts varies during this period from 80 to 460 km for the STC, 140 to 340 km for the SAC and 60 to 190 km for the APF (Valentine and Lutjeharms, 1983). The subtropical convergence, the northernmost of the fronts, is characterized by a large temperature gradient, i.e., 5°C to 10°C in less than 2° of latitude. At this front, located at about 40°S, the subantarctic water moving north-eastward sinks

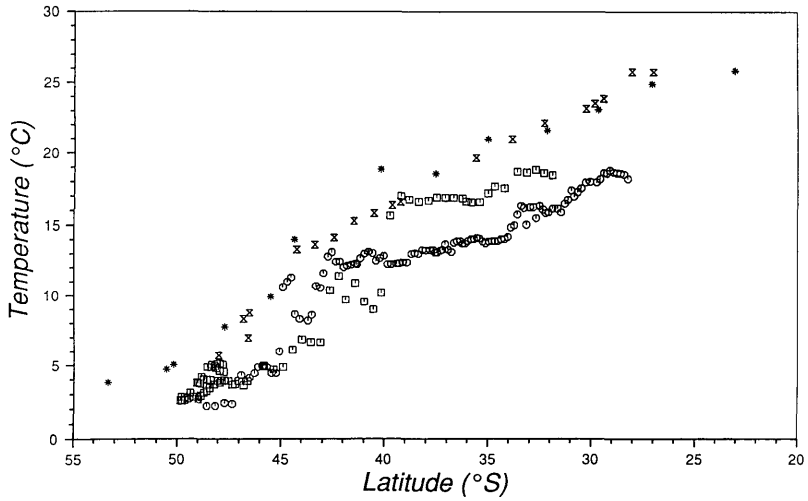

Fig. 4. Observed temperature versus latitude. ⊙ Eastern track in July 1984. □ Western track in July 1984. X Eastern track in February–March 1985. * Western track in February–March 1985.

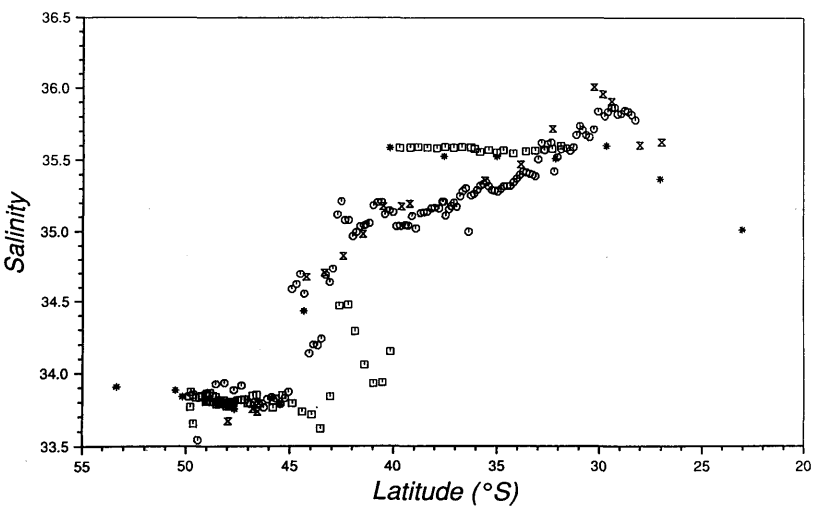

Fig. 5. Observed salinity versus latitude. ⊙ Eastern track in July 1984. □ Western track in July 1984. X Eastern track in February–March 1985. * Western track in February–March 1985.

below the subtropical water moving southward. The subantarctic front which is not clearly recognizable with sea surface parameters is generally located about 5° north of the antarctic polar front (Valentine and Lutjeharms, 1983). The latter, located near 50°S separates the cold antarctic surface water from the warmer (about 2°C) and less saline subantarctic surface water.

In order to locate these fronts during the two INDIVAT cruises, temperature, salinity and oxygen are plotted against latitude for both the eastern and western tracks (Figs. 4, 5 and 6). For the sake of clarity and since both (eastern and western) tracks present many similarities, the next discussion will focus on only the eastern track results.

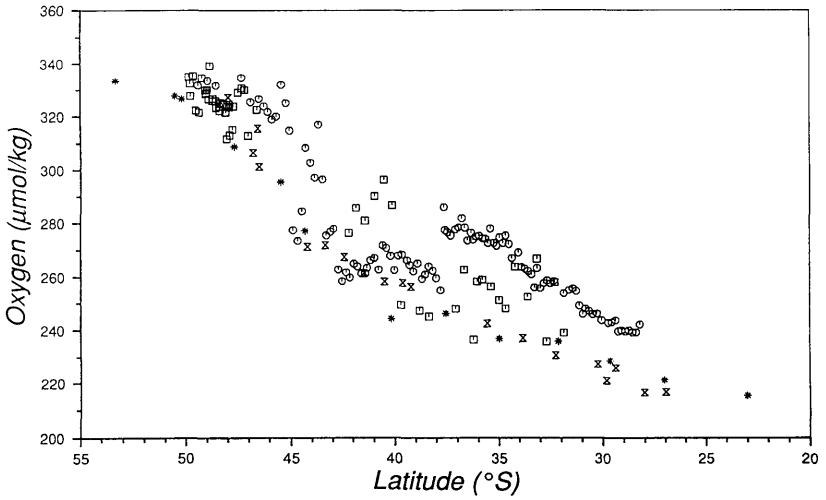

Fig. 6. Observed oxygen concentration versus latitude. ⊙ Eastern track in July 1984. □ Western track in July 1984. X Eastern track in February–March 1985. * Western track in February–March 1985.

5. Parameters of the CO_2/carbonate system

Measured and computed pCO_2 values for seasurface water between Kerguelen, Amsterdam, and Réunion islands are plotted versus latitude in Figs. 7a and 7b. The difference between Figs. 7a and 7b shows the random differences of pCO_2 between values directly measured and those calculated from the measured pair TA-TCO_2 which have been discussed above. The first notable feature in the results of July 1984, is the decrease in pCO_2 values from approximately 340 µatm at 29°S to about 315 µatm at 33°S, followed by a continuous increase up to approximately 360 µatm near Kerguelen island at 49°S. The pCO_2 in surface waters reached equilibrium with atmospheric pCO_2 value at around 42°S.

Data of pCO_2 collected in February–March 1985 on the same transect is also plotted versus latitude in Fig. 7. From about 28°S to 36°S, pCO_2 in surface waters was almost in equilibrium with atmospheric values, before decreasing to 310 µatm at 40°S and then increasing almost linearly up to 350 µatm at 47°S. The atmospheric pCO_2 value (343 µatm in dry air) shown in Figs. 7a and 7b is in good agreement with those measured in dry air on Amsterdam island at the time of the cruises (Gaudry, personnal communication).

Fig. 8 is a plot of the measured total inorganic carbon of the seasurface waters from these two cruises (July 1984 and February–March 1985) on the same transect Kerguelen, Amsterdam, and Réunion islands, versus latitude. In July 1984, TCO_2 is almost constant at 2060 µmol kg^{-1} from around 33°S to 45°S before increasing linearly up to 2140 µmol kg^{-1} at 49°S. Though this feature is similar in March 1985, we observed higher values in July 1984 than in March 1985. The largest difference (30 µmol kg^{-1}), is located between the Subtropical and Antarctic convergences.

The TA values determined on the same cruise track in July 1984 and March 1985, are represented versus latitude in Fig. 9. Except almost constant TA observed in July 1984 between latitudes 28°S and 42°S, TA decreases continuously with increasing latitude. These data show higher TA values in February–March 1985 than in July 1984, with a difference up to 35 µeq kg^{-1} between 30°S–40°S.

The comparison of the seasurface data normalized to 35 salinity, from different years (February 1978 from GEOSECS data and March 1985) does not suggest any detectable increase in TCO_2 concentration. At all stations, TCO_2 values were virtually unchanged (1945.3 in February 1978 and 1945.7 in March 1985 at 27°S, and 2172.0 in February 1978 and 2172.2 in March 1985 at 48°S), and certainly do not reflect the expected

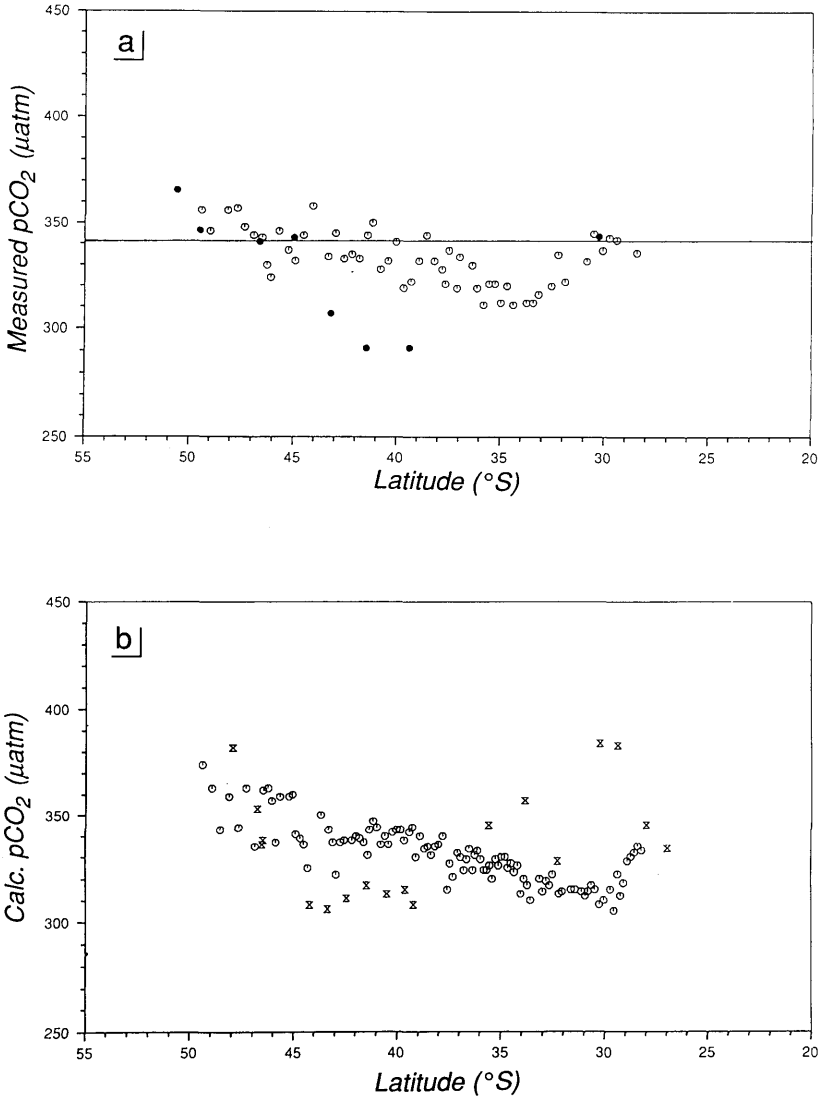

Fig. 7. (a) Measured pCO_2 versus latitude. ⊙: Eastern track in July 1984. X: Eastern track in February–March 1985. (b) Calculated pCO_2 versus latitude. ⊙: Eastern track in July 1984. X: Eastern track in February–March 1985.

TCO_2 increase of almost $1\ \mu mol\ kg^{-1}\ yr^{-1}$ (N.A.S, 1983). This unexpected observation is likely to be the result of the difference in the accuracy of the measurements. During these two cruises, TCO_2 was determined by potentiometric titration with similar standards. Even if the apparent dissociation constants of carbonic acid used for the calculations were not the same (the final corrected TCO_2 values of the GEOSECS program were computed using the constants of Mehrbach et al., (1973) while those of the INDIVAT/INDIGO program were computed using the recommended equations (UNESCO, 1987) given by Dickson and Millero (1987)), the difference in computed TCO_2 due to the difference between the two sets of constants is smaller than

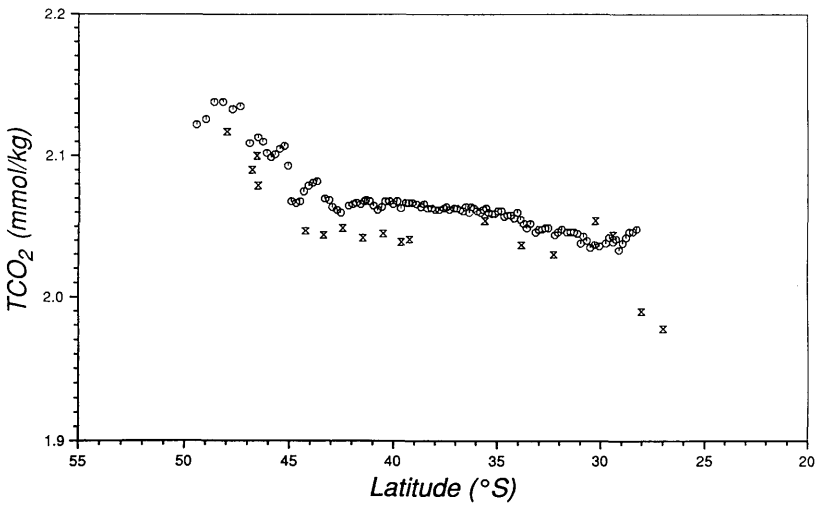

Fig. 8. Measured Total CO_2 versus latitude. ⊙: Eastern track in July 1984. X: Eastern track in February–March 1985.

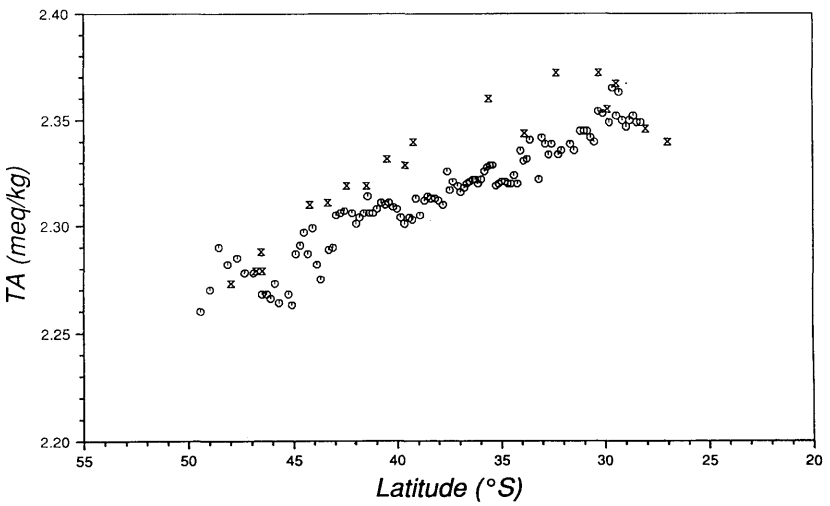

Fig. 9. Measured total alkalinity versus latitude. ⊙: Eastern track in July 1984. X: Eastern track in February–March 1985.

0.5 μmol kg^{-1}. On the other hand, according to both the DOE report on the GEOSECS carbon dioxide results (Östlund and Dyrssen, 1980) and Bradshaw et al. (1981), the blanks were poorly known for GEOSECS measurements and 10 μmol kg^{-1} is easily possible as un uncertainty.

Assuming both that CO_2 exchanges between sea surface water and the atmosphere are very fast compared to those between sea surface water and the deep ocean (Peng and Broecker, 1985), and that this region of the ocean (between 35°S and 48°S) is a strong sink for atmospheric fossil fuel CO_2 (Broecker et al., 1986), the difference in TCO_2 between 1978 and 1985 should be much larger than 7 μmol kg^{-1}, which represents only a mean value for the global ocean. This significant amount which was not detected by the present TCO_2 measurements point out the need to better understanding, and to improve the accuracy of the determination of the main parameters (TCO_2, TA and pCO_2) of the carbonate system in sea water.

6. Discussion

Over most of the ocean, pCO_2 variations are mainly due to seasonal temperature and salinity changes. Weiss et al., (1982) have shown that pCO_2 variations in the tropical Pacific ocean between 15–20°N and 14–17°S, are for the most part, a response to seasonal variations in the temperature and salinity of sea surface waters, rather than to CO_2 transfers through physical or biological processes. Nevertheless, over considerable areas, significant biological activity, which decreases TCO_2 and consequently also pCO_2 (Jacques and Treguer 1986, Berger et al., 1986), is likely to be a major contributor to the seasonal variations in pCO_2.

From July 1984 to March 1985, observed pCO_2 values in the upper layer of the Southwest Indian ocean increase north of approximately 36°S, whereas south of approximately 36°S, they decrease. During the same period, at all latitudes, the temperature increases by more than 3°C. These observations strongly suggest that the temperature predominates north of approximately 36°S. Southward, both physical mixing and biological processes produce very large pCO_2 variations, and not only mask those induced by temperature changes, but also decrease sea surface pCO_2.

In order to evaluate the pCO_2 variation caused by a change of temperature in a closed system, a simple calculation using a constant property pair TCO_2-TA leads to a pCO_2 increase of 65 μatm at location 33°S, 45°E when the temperature increases by 5°C from July 1984 to March 1985. The observed value, which reflects the variation of pCO_2 of an open system indicates a pCO_2 increase of 45 μatm. The amplitude of this observed increase indicates that the pCO_2 variations due to mixing and gas exchange dominates those due to biological activity. On the other hand, south of 35°S, a similar calculation leads to a pCO_2 increase of 15 μatm where we observed a pCO_2 decrease of 30 μatm. Here, since the observed pCO_2 decreased, the seasonal biological activity is probably the driving process that endows the pCO_2 increase due to warmer seawater.

The low pCO_2 values (down to 30 μatm below the atmospheric pCO_2 value) observed in March 1985 between 35°S and 45°S in the Southwest Indian ocean are in agreement with general observations, which would indicate that there is a latitudinal band located between 40°S and 55°S where oceanic surface pCO_2 values are well below atmospheric pCO_2 (a difference larger than 30 μatm according to Takahashi and Chipman, 1985). These authors indicate that pCO_2 values drop in response to a temperature decrease caused by warm waters (poor in nutrients) which cool down when moving southwards, and CO_2 photosynthetic consumption in cold water enriched in nutrients. They estimated that about 20% of the CO_2 injected into the atmosphere by industry could invade the ocean in this area.

In July 1984, observations within the same latitudinal band showed pCO_2 values close to equilibrium with the atmospheric pCO_2 value, thus suggesting that most of the atmospheric CO_2 which penetrates in this oceanic area, penetrates during summertime.

Between 45°S and 55°S both in July 1984 and March 1985, the observed sea-surface pCO_2 values indicate that the southwest Indian ocean was a source of CO_2 for the atmosphere. These high pCO_2 values observed south of the Antarctic front may seem surprising if we refer to the most recent world map of the difference in pCO_2 values between the atmosphere and sea surface waters (Broecker et al., 1986). They calculated a mean difference of 20 μatm in the area we have studied. Nevertheless, our pCO_2 data agree with those of the GEOSECS program in the southwest Indian ocean and Antarctic ocean. Gammon et al., (1985) also observed that in regions where convective mixing occurs, deep waters with high CO_2 concentrations which reach the surface may create a source of CO_2 for the atmosphere. Furthermore, they demonstrated that most of these areas are found in the southern hemisphere, south of the circumpolar current. Like earlier observations of high pCO_2 values in the South Pacific ocean (Miyake et al., 1974) and in the southeast Indian Ocean (Inoue and Sugimura, 1988), our results give a new confirmation of these phenomena. Our data also support earlier atmospheric ^{14}C results that suggest a strong ocean-atmosphere interaction in the region between 50°S and 70°S (Levin et al., 1987). Thus, this southern part of the ocean seems to be a source of CO_2 for the atmosphere throughout the year.

7. Conclusion

In order to estimate the mean annual CO_2 flux across the air-sea interface, one must know the transfer coefficient, and the difference in partial pressure of CO_2 across the interface. Presently, the transfer coefficient can be calculated (with an accuracy better than 30%) from the wind velocity at 10 meters, using the relationships suggested either by Liss and Merlivat (1986) or by Peng and Takahashi (in press). These latter are based on 14C measurements and give higher results than the former. It is still however, the paucity of the data set of the difference between atmospheric and seasurface pCO_2 that strongly limitates the accuracy of the estimation of CO_2 fluxes across the air-sea interface. Although we fail to detect the expected interannual increase of TCO_2 because of inaccuracy in the earlier determination of the parameters of the CO_2/carbonate system, poor knowledge of the horizontal and vertical carbon fluxes within the ocean, and the small size of the anthropogenic signal relative to experimental error and local variability, these new observations significantly increase the CO_2 data set of the southwest Indian ocean. The comparison of measured seasurface pCO_2 between July 1984 and February–March 1985 suggest that north of 35°S, the seasonal variation of sea surface pCO_2 is primarily controlled by the seasurface temperature whereas it is predominantly regulated by the seasonal biological activity from approximately 35°S to 45°S. Farther south, down to at least 50°S, this part of the ocean is likely to be a source of CO_2 for the atmosphere.

8. Acknowledgements

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