

DOE/ER/61397--1

DE92 040334

ANNUAL PROGRESS REPORT

submitted to

CARBON DIOXIDE RESEARCH PROGRAM

OFFICE OF HEALTH AND ENVIRONMENTAL RESEARCH, ER-76

THE DEPARTMENT OF ENERGY, WASHINGTON, D. C. 20545

Measurements of Carbon Dioxide

in the Southern Ocean along the WOCE S-4 Section

David W. Chipman, Stephany I. Rubin, Taro Takahashi

Lamont-Doherty Geological Observatory

Columbia University, Palisades, NY 10964

This report was an account of work sponsored by the United States Government. Neither the United States, nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warantee, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

August, 1992

Prepared for

THE US DEPARTMENT OF ENERGY

AGREEMENT NO DE-FCO2-92ER61397

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

L-DGO Proposal No. 6797

ABSTRACT

During the first year of this two-year grant, we have completed the data acquisition phase at sea along the WOCE-S4 section located along 67°S between 73°W and 172°E in the Pacific sector of the Southern Ocean. The expedition was carried out aboard the Russian Research Ship "Akademik IOFFE" in the period February 14 through April 6, 1992. The total CO₂ concentration and pCO₂ in a total of about 1290 water samples were determined using a coulometer for total CO₂ and an equilibrator/gas chromatograph system for pCO₂. Surface water samples were analyzed at all the 112 hydrographic stations occupied. Complete or partial profiles were obtained at 58 stations. In addition, a total of 172 determinations were made at sea for 62 bottles of the Standard Reference Solution (Batch #7), yielding an average value of 1927.5 ± 1.8 $\mu\text{mol/kg}$. This compares with the SIO manometric value of 1925.74 ± 0.74 $\mu\text{mol/kg}$ (9 determinations). Sources for the systematic difference are being investigated.

The surface water data show that the SST was nearly constant at about 1.0°C over the 67°S section and that, with a exception of two narrow zones, the surface water was undersaturated with respect to atmospheric CO₂ by about -30 μatm . The surface water was supersaturated with respect to atmospheric CO₂ by as much as +15 μatm within the two zones, 121°W-128°W and 150°W-160°W. This may be attributed to a local upwelling of deep water. The deep water data show that the total CO₂ concentration along the section is nearly uniform below about 400 meters and tends to increase from west to east: 2250 $\mu\text{mol/kg}$ at 72°W to 2265 $\mu\text{mol/kg}$ at 160°W.

1. INTRODUCTION

This is a second year continuation proposal for the two-year study "Measurements of Carbon Dioxide in the Southern Ocean along the WOCE S-4 Section", which is funded for a period of March 1, 1992 through February 28, 1993. The purpose of this funded study is to determine the distribution of the total CO_2 concentration and pCO_2 in the Southern Ocean along the WOCE S-4 section. Since there are virtually no CO_2 data available in the high latitude Pacific sector of the Southern Ocean, the data obtained during this study will significantly contribute to the global data base of the oceanic carbon dioxide. The field work at sea, which was proposed for the first year, has been completed, and the investigation is progressing as planned in the original proposal. The progress made to date is described in this report.

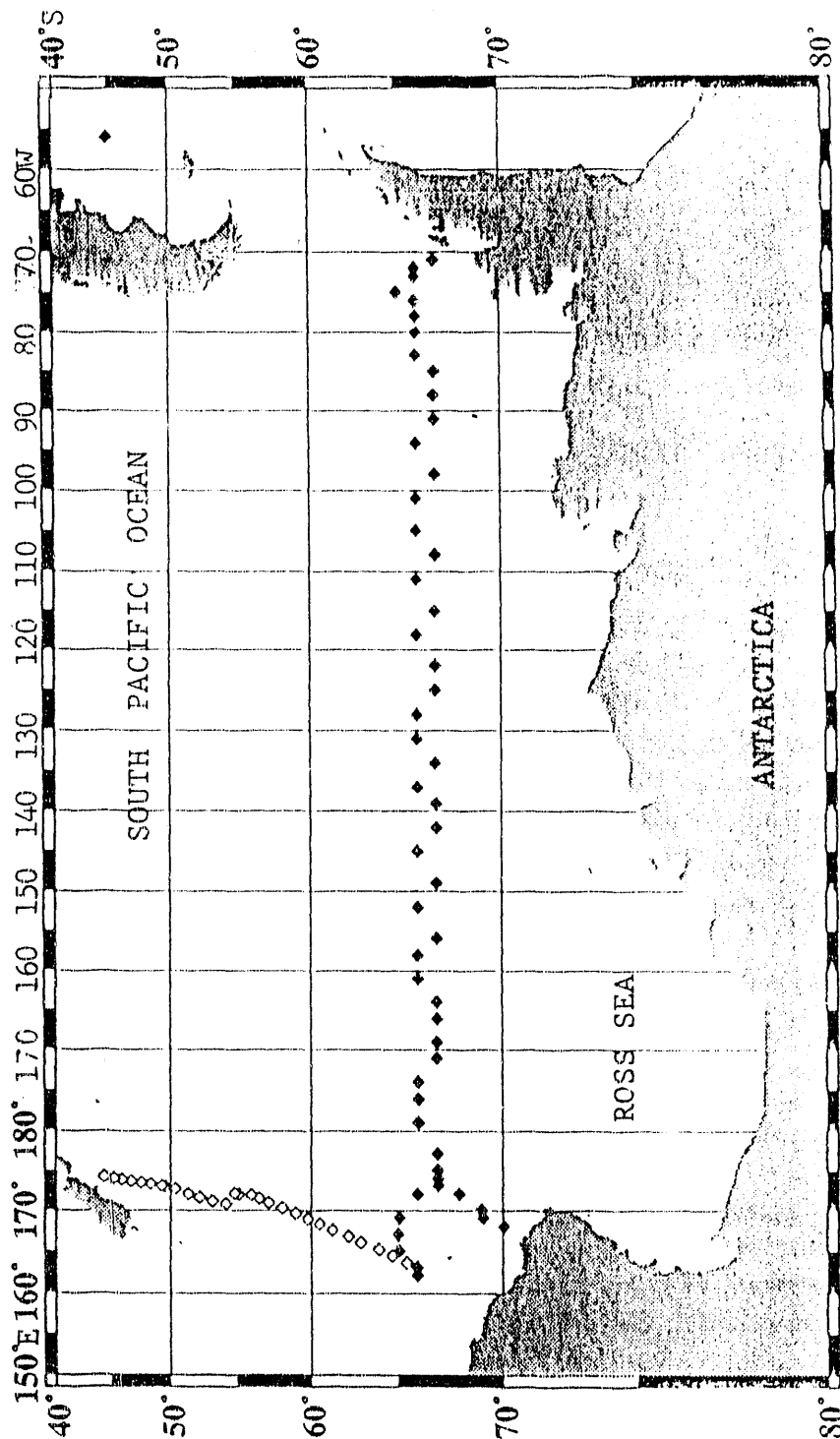
2. PROGRESS TO DATE

The field phase of this investigation started from Montevideo, Uruguay, on February 14, 1992, aboard the Russian Research Ship "Akademik IOFFE" and completed at Wellington, New Zealand, on April 6, 1992. A total of 112 hydrographic stations (24 discrete bottle samples per station) were occupied along the main E-W section at 67°S between about 72°W and 172°E and a N-S mini-section toward the Ross Sea along 168°E between 67°S and 70.65°S in the Pacific sector of the Southern Ocean. Station locations are shown in Fig. 1. During the 50-day expedition, 1291 water samples were analyzed for the total CO_2 concentration using a coulometer, and 1287 water samples were analyzed for pCO_2 using an equilibrator-gas chromatograph system. Approximately 10% of the total CO_2 measurements were made in duplicates; all the pCO_2 measurements were made at 4 °C at least in duplicates or often in triplicates. Therefore, the actual number of analyses performed at sea exceeded a total of 4500. In addition, 172 determinations were made for the Standard CO_2 Reference Solutions (Batch #7), and about 100 air samples were analyzed for CO_2 .

2.1 Calibration of Coulometer:

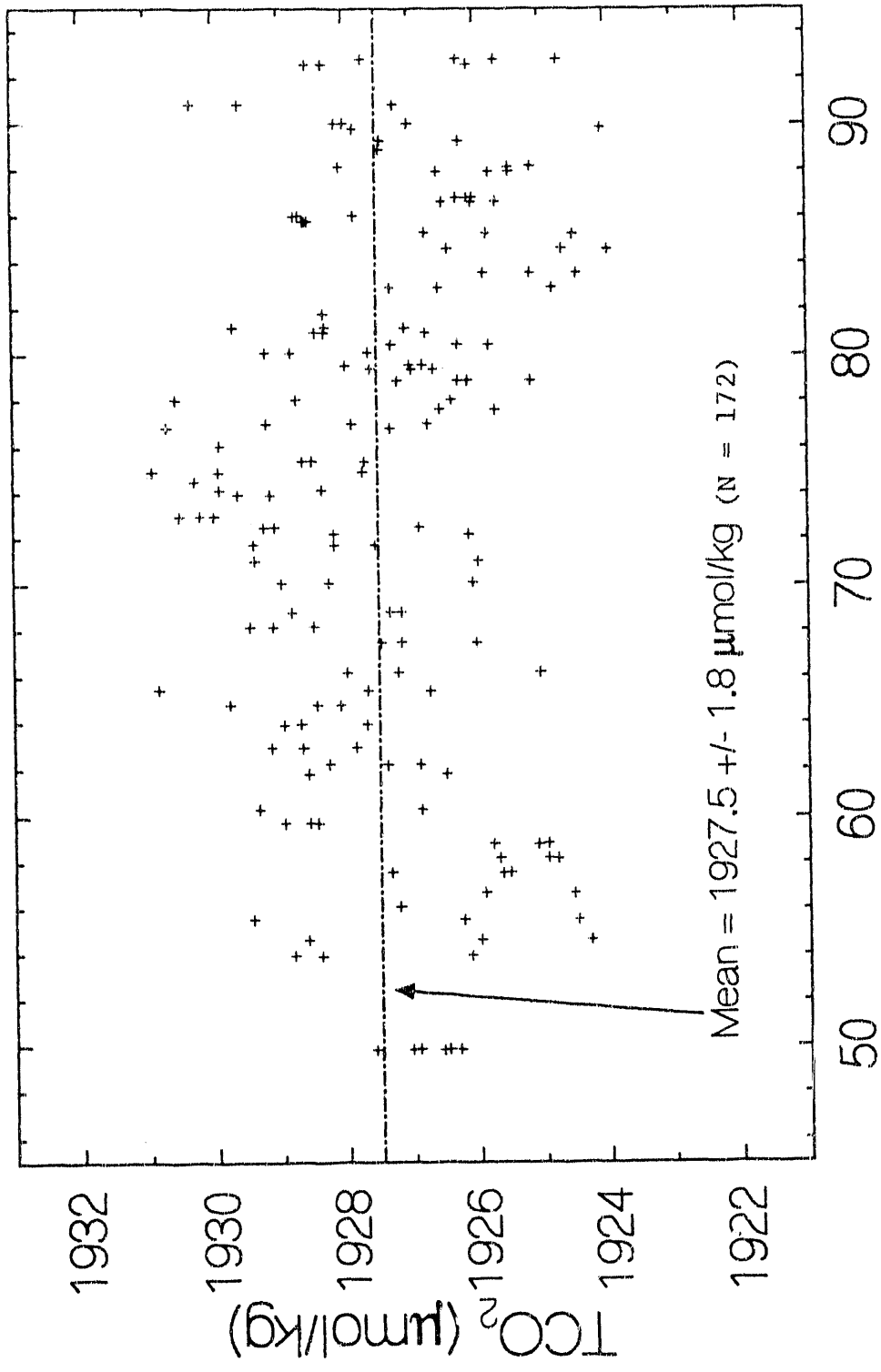
The coulometer for the total CO_2 concentration measurement was calibrated several times a day using a gas pipette of known volume which was filled with pure CO_2 gas (99.9998%) at a known temperature and pressure. In order to evaluate the performance of our coulometer and allow our data to be compared with those obtained by others, the total CO_2 concentration in the Standard CO_2 Reference Solutions (Batch #7) provided by Andrew G. Dickson of the Scripps Institution of Oceanography was determined a few times daily. The results of our measurements made during the expedition are shown in Fig. 2. Our preliminary data give a mean total CO_2 concentration of 1927.5 ± 1.8 $\mu\text{mol/kg}$ for 172 determinations (from 62 bottles of the Reference Solutions). This compares with the mean of the nine (9) manometric determinations of 1925.74 ± 0.74 $\mu\text{mol/kg}$ made at the

Fig. 1 - Station locations for the WOCE S-4 expedition of the Russian Research Ship "Academik IOFFE", February 14 - April 6, 1992. The filled symbols indicate the stations for surface-to-bottom profiles and the open symbols indicate the stations for surface samples only.



FILED JUN 29 17:39

Fig. 2 - The results of the coulometric determination of total CO₂ concentration in the Standard CO₂ Reference Solutions, Batch #7.
WOCE-S4 SRM's Batch #7



shore-based laboratories of C. D. Keeling, Scripps Institution of Oceanography. Although the difference between these two mean values of 1.8 $\mu\text{mol/kg}$ is within one standard deviation of the LDGO data, the data are being further examined for possible sources of systematic errors.

2.2 Surface Water Data:

The preliminary data obtained in the surface water along 67°S between 72°W and 172°E are summarized in Fig. 3. The surface water temperature was nearly uniform at about 1.0 ± 0.2 °C nearly all the way along the section with an exception of west of the date line, where temperatures as low as -0.9 °C were observed. A broad minimum of salinity (as low as 33.4 o/oo) was centered around 130°W, and the salinity increased to the east and west to about 33.9 o/oo. The total CO_2 concentration followed the distribution pattern of the salinity, ranging from about 2170 $\mu\text{mol/kg}$ when salinity was high (33.9 o/oo) to 2115 $\mu\text{mol/kg}$ when salinity was low (33.4 o/oo). This suggests that changes in the total CO_2 concentration in surface waters are largely attributable to the water balance. The alkalinity values which have been computed using the total CO_2 and pCO_2 values also follow the salinity changes.

The surface waters along 67°S are generally undersaturated with respect to atmospheric CO_2 by about -30 uatm on the average. However, in two narrow zones, 120°W-128°W and 150°W-161°W, the ocean is supersaturated by as much as +15 uatm, and hence these areas are a source for atmospheric CO_2 (see the fourth panel from the top in Fig. 3). The high concentrations of total CO_2 and nutrient salts observed in these areas indicate that these CO_2 source areas are due to local upwelling of deep waters rich in CO_2 and nutrient salts. Furthermore, since the low pCO_2 values are well correlated with low concentrations of nutrient salts, the oceanic CO_2 sink areas may be largely attributed to photosynthesis.

2.3 Total CO_2 Distribution in Deep Ocean:

While the total CO_2 concentration in surface waters varied by as much as 60 $\mu\text{mol/kg}$ along the 67°S section, it varied only by 15 $\mu\text{mol/kg}$ below about 400 meters, ranging from 2250 to 2265 $\mu\text{mol/kg}$ (see Fig. 4). The lower values have been found to the east. The observed magnitude of variation and the distribution pattern for the total CO_2 concentration are broadly consistent with those found for the dissolved oxygen concentration which varied from 195 $\mu\text{mol/kg}$ in the east to 220 $\mu\text{mol/kg}$ to the west.

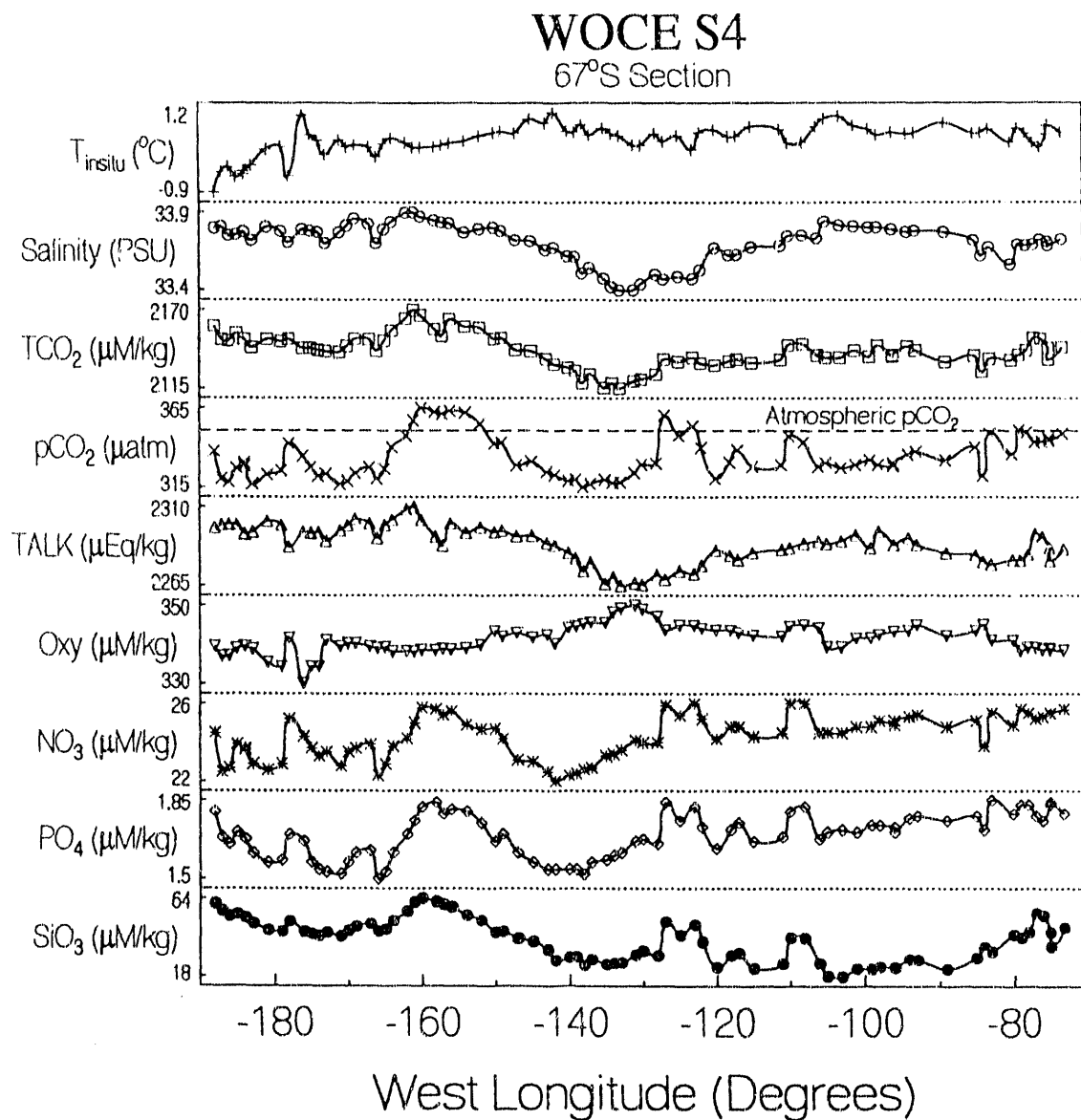


Fig. 3 - The temperature, salinity and other chemical properties in surface waters along the 67°S parallel (WOCE S-4) observed in February through April, 1992.

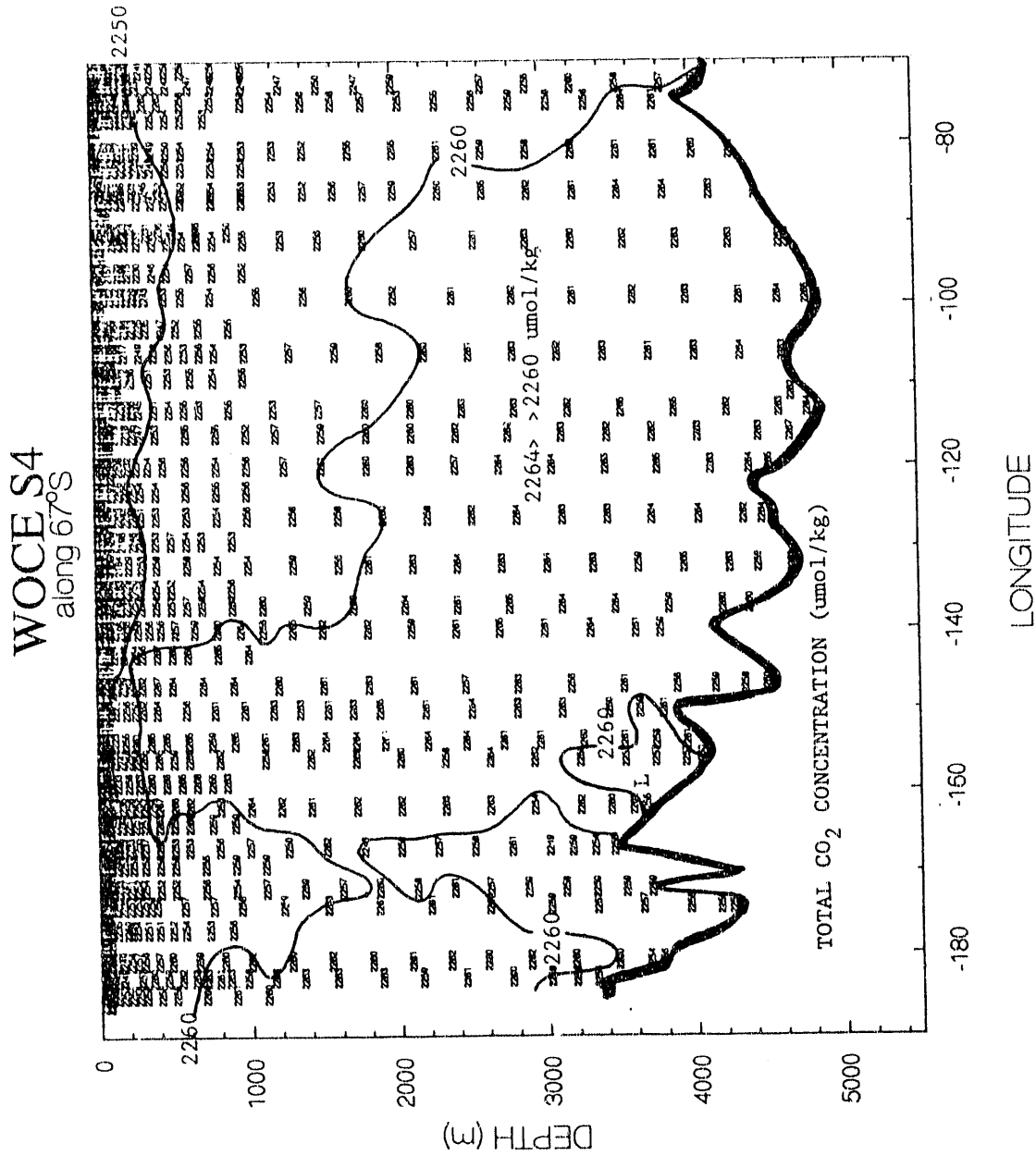


Fig. 4 - Distribution of the total CO₂ concentrations in the Pacific sector of the Southern Ocean along 67°S, WOCE Section S-4.

END

DATE
FILMED

10 / 20 / 92

