

6. Inorganic carbon cycling in the Crozet area

6.1 Leg 1 D285

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Rationale



Iron supply and air-sea exchange of carbon dioxide (CO₂) are closely linked in the Southern Ocean. The current understanding is that low iron concentrations limit algal growth in HNLC waters. Seasonal algal blooms downstream of islands and in frontal jets reduce the CO₂ concentration in the mixed layer (Bakker et al., 1997). The overall primary productivity in the Southern Ocean may be higher than satellite observations suggest (Schlitzer, 2002). It is not clear where this 'extra' production occurs: HNLC waters might be less widespread or more productive than the satellite observations indicate. Or, algal growth in iron-replete waters has been under-estimated.



The Southern Ocean is an important area for ventilation of the deep ocean and for uptake of anthropogenic CO₂. Deep water comes to the surface and exchanges heat, CO₂, and other gases with the atmosphere before descending again. Estimates of net oceanic CO₂ uptake south of 50°S for ~1995 range from 0.1-0.5 Pg C yr⁻¹ (Pg = 10¹⁵ g) (Rayner et al., 1999; Takahashi et al., 2002), 6-29% of the net global oceanic uptake of the greenhouse gas (Prentice et al., 2001). Most of the anthropogenic CO₂ taken up by the Southern Ocean is transported north along equal density surfaces (Caldeira and Duffy, 2000), presumably in Antarctic Intermediate Water and Subantarctic Mode Water (Sloyan and Rintoul, 2001). A reduction of the vertical mixing and upwelling in the Southern Ocean would probably increase the atmospheric CO₂ level (Sarmiento et al., 1998; Matear and Hirst, 1999). Such circulation changes could also reduce the supply of iron from shallow topography to surface waters, which would further limit algal growth and would equally increase the atmospheric CO₂ level. Global warming might provoke such changes in the circulation of the Southern Ocean (Sarmiento et al., 1998).

Objectives

- Assess the importance of natural iron fertilisation from shallow topography for the marine CO₂ sink near the Crozet Plateau.
- Quantification of a carbon budget for the Crozet blooms.
- Comparison of the effects of natural and anthropogenic iron fertilisation on oceanic CO₂ uptake.
- Determine potential applications of satellite observations for quantifying oceanic CO₂ uptake.

With the additional objectives:

- Assessment of CO₂ air-sea transfer between the Crozet Plateau and South Africa.
- Better quantification of the air-sea gas transfer velocity.

Methods

Underway parameters: oxygen and pCO₂

The seawater supply –The ship's seawater supply provided large volumes of water for underway sampling. The seawater temperature was measured at the water intake at 6.5 m depth in the ship's bow. A centrifugal pump transported the water to the laboratories. The water was fed through a debubbler. The salinity of the water was measured. In the chemistry laboratory the seawater passed an oxygen sensor, a strainer with a bypass, and finally the equilibrator for pCO₂ analysis. The bypass was used for discrete sampling of oxygen, dissolved inorganic carbon (DIC), and alkalinity.

The partial pressure of CO₂ in surface water and marine air - Continuous measurements of pCO₂ in surface water and marine air were made throughout the cruise with the underway CO₂ system designed by Ute Schuster (UEA) (CAVASSOO, 2004). Marine air was collected through tubing from the foremast. Seawater from the ship's surface water supply was introduced at a rate of 3 l min⁻¹ into a fast response equilibrator with a showerhead (Bakker et al., 2001). A Pt100 probe accurately determined the water temperature in the equilibrator. A vent kept the headspace of the equilibrator at atmospheric pressure. Every minute the CO₂ content and the moisture content of the headspace were determined by an infrared LI-COR 6262 analyser. The analysis of the CO₂ content in the headspace was interrupted for that of the CO₂ content in marine air (20 minutes per 6 hours) and in two CO₂ standards (30 minutes per six hours each). Samples from the equilibrator headspace and marine air were partly dried to 10°C below the ambient temperature in an electric cool-box. The standards of 266.6 (later 267.7) and 481.0 μmol CO₂ mol⁻¹ (σ of 0.5 μmol mol⁻¹) had been calibrated against certified NOAA standards. The analyses were carried out for a flow speed of 100 ml min⁻¹ through the LI-COR at a slight overpressure. A final analysis for each parameter was made at atmospheric pressure with no flow. The flow and overpressure did not have a discernable effect on the CO₂ and moisture measurements, once the pressure had been corrected for. The correction by Takahashi et al. (1993) was used to correct for warming of the seawater between the ship's water intake and the equilibrator. Here warming of the seawater was taken as 0.4°C. The pCO₂ measurements were time stamped by GPS. The time delay between sampling and analysis will be taken as 4 minutes for pCO₂ in air and surface water. The precision and accuracy of the pCO₂ data was approximately 1.0 μatm, as determined in previous cruises (Bakker et al., 2001).

The final pCO₂, DIC, alkalinity, and O₂ data will be stored with other cruise data at the British Oceanographic Data Centre (<http://www.bodc.ac.uk/>). Initially the data will be accessible to cruise participants only. The data will become publicly accessible once the results have been published. Surface water pCO₂ data will also be submitted to the international, publicly accessible surface water pCO₂ database at the U.S. Carbon Dioxide Information Analysis Center (<http://cdiac.esd.ornl.gov/oceans/>).

The oxygen concentration of surface water – The oxygen (O₂) concentration and water temperature were measured with an optode, model 3930 from Aanderaa (Figure 6.1a). The oxygen measurement is based on dynamic luminescence quenching of luminophore molecules (platinum porphyrine) embedded in a sensing foil, which is exposed to the surrounding water (Aanderaa, 2003). A light emitting diode (LED) and a photo-diode are

placed on the instrument side of the foil. Absorption of a photon from the blue-green photo-diode excites the luminophore molecules in the foil. If a luminophore molecule does not collide with another molecule, it will return to its initial state by emitting a photon. The photo-diode detects the quantity of this fluorescent light. However, if a luminophore molecule collides with an O₂ molecule, it transfers its excitation energy to the oxygen molecule. The intensity of fluorescent light thus decreases with the oxygen concentration.

The instrument is in a cylindrical titanium housing with a length of 160 mm and a diameter of 40 mm. A purpose built titanium housing positioned the optode in the seawater flow (Fig. 6.1b). The optical window of the optode was in the wider part of the housing and in the centre of the flow. The external housing was positioned vertically, as in Fig. 6.1b. The optical window of the optode was put in the direction of the flow, in order to minimize any effects from air bubbles. The temperature sensor just entered the wider part of the external housing. A 10 pin cable with a small split cable fitting connected the optode to the temperature and oxygen channels on the datalogger, model 3660 from Aanderaa. The data from the optode were logged on the datalogger and passed on every minute to the laptop of the online pCO₂ system.

The optode has a measuring range of 0-500 µM for oxygen, with a resolution better than 1 µM and an accuracy better than 8 µM or 5%, whichever is greater (Aanderaa, 2003). The optode is valid for a salinity range of 33-37. Software in the data logger calculates the oxygen concentration (µM) from the raw data and the calibration coefficients of the oxygen sensor. The oxygen optode has its own internal thermometer for the calculation of the oxygen concentration in addition to the external temperature sensor.

The optode provided oxygen concentrations in freshwater, which were corrected to a constant salinity of 33.8, while assuming warming of 0.4°C between the seawater inlet and the optode (Aanderaa, 2003). Preliminary values for the oxygen saturation in seawater were calculated using the equations by Garcia and Gordon (1992). The oxygen data will be recalculated for the correct seawater temperature and salinity and will be checked against oxygen concentrations determined by the Winkler method in surface samples from the CTD (Richard Sanders and colleagues) and the ship's seawater supply.

The temperature range for the external temperature sensor is -7.5 to +41°C with an accuracy of ±0.1°C and a resolution of 0.05°C. The temperature readings of the optode showed an offset of several degrees Celsius relative to the temperature in the equilibrator. Earlier study of this problem (Nielsdóttir, 2004) suggests that the temperature sensor is outside the main flow of the water. These temperature data will not be discussed further.

Vertical profiles of DIC and alkalinity

CTD sampling – Samples for the analysis of DIC and alkalinity were collected in 500 ml glass bottles from the 20 l Niskin bottles on the CTD rosette. The 25 standard CTD casts were sampled, as well as 5 thorium casts (15495, 15498, 15539, 15540, 15548). The standard CTD casts were sampled to the bottom, except at station 15489 (J). Typical sampling depths were 10 m, 20 m, 40 m, 60 m, 80 m, 100 m, 150 m, 200 m, 300 m, 400 m, 500 m, 750 m, 1000 m, 1500 m, 2000 m, 2500 m, 3000 m, 3500, bottom – 10 m, while leaving out depths, if the water column was shallower. Thus, approximately 400 CTD samples were analysed for DIC and alkalinity. Samples were also taken from the

ship's surface water supply to increase spatial coverage: 297 samples for DIC and 199 for alkalinity.

Generally samples were analysed within 24 hours of collection. If this could not be achieved due to instrument failure (DIC) or close station spacing, the samples were fixed by adding 100 μl of a saturated mercury chloride solution for each 500 ml sample. Fixed samples were stored in the dark in a cold room (5°C). All samples were analysed within 6 days of collection.

Dissolved inorganic carbon – Samples were kept cold before measurement in a seawater flow. The DIC concentration was determined by coulometric analysis after the method of Johnson et al. (1987). At least three replicate analyses were made on each sample bottle, until two replicates were within $1 \mu\text{mol kg}^{-1}$ (100 counts) for a blank below $0.3 \mu\text{mol kg}^{-1} \text{min}^{-1}$ ($30 \text{ counts min}^{-1}$). The system had a small carry over effect, such that the first replicate of a sample was discarded, if a strong DIC change occurred between samples and between samples and standards. The instrument was kept running, except when the cell was changed, as this gave the best results. Generally all samples from one cast and sometimes a few samples of another cast were run per cell. The starting up time for a new cell varied from 2 to 8 hours, before the blanks came down sufficiently. The temperature of the samples during analysis was determined with an accurate Pt100 sensor.

At least one standard of certified reference material from batches 65 and 66 (DOE, 1994) was used per coulometric cell and per cast. The specifications of batch 65 were:

salinity	33.049
DIC	$1993.68 \mu\text{mol kg}^{-1} \pm 0.32 \mu\text{mol kg}^{-1}$
total alkalinity	$2206.00 \mu\text{mol kg}^{-1} \pm 0.68 \mu\text{mol kg}^{-1}$
phosphate	$0.40 \mu\text{mol kg}^{-1}$
silicate	$1.0 \mu\text{mol kg}^{-1}$
nitrite	$0.03 \mu\text{mol kg}^{-1}$
nitrate	$0.14 \mu\text{mol kg}^{-1}$.

Batch 66 awaits certification.

From 26-28 November the instrument blank stayed above 30 counts per minute, just as a new nitrogen cylinder of a 4.6 quality was started. During trouble shooting many components of the system were replaced: new coulometer chemicals, fresh soda lime from a new pot, a new 4.5 quality nitrogen gas cylinder, a clean extractor for the extractor unit, and a new lamp for the coulometer. Exclusion of the extractor unit from the system showed that the blank problem originated from the carrier gas, the soda lime, the coulometer, or the cell. The carrier gas and ineffective soda lime were the most likely source of the blank problem. The blanks came down after the trouble-shooting.

Organic particles and possibly dissolved organic matter affected the analysis of some samples from the upper 1000 m. We estimate a precision and an accuracy better than $2.7 \mu\text{mol kg}^{-1}$ after Bakker et al. (2001). The data await processing and careful analysis.

Alkalinity – The alkalinity measurements were made by potentiometric titration with a VINDTA instrument (#4, version 3C) developed by Ludger Mintrop (2004). The acid consumption up to the second endpoint is equal to titration alkalinity. The system uses a Metrohm Titrino 719S, an ORION-Ross pH electrode and a Metrohm reference electrode. The burette, the pipette (volume 99 ml), and the analysis cell have a water jacket around them.

Samples were kept at room temperature (~18°C) before measurement. The water jackets and two samples, one awaiting analysis and the other being analysed, were kept at a constant temperature of 24.5°C by a recirculation water bath. The temperature was checked regularly by a calibrated mercury thermometer. The titrant (0.1M hydrochloric acid, HCl) was made by dilution of 50 ml of 1 M HCl with 450 ml of MilliQ. Three different batches of titrant were used.

Two or three replicates were run on each sample bottle, until the difference between two replicates was less than 1 $\mu\text{mol kg}^{-1}$. The first measurement after restarting the system, a pause in the analysis, or after topping up the electrodes was generally slightly off and was discarded. The instrument was occasionally affected by a carry over effect if there were large differences in alkalinity between successive samples or between samples and the seawater standards. At least one standard of batches 65 or 66 was run per CTD cast, generally after they had been used for DIC analysis. Occasionally a new standard was opened for alkalinity. The alkalinity data need correction for seawater density and nutrient concentrations. The data await careful analysis.

Results

The data shown here are preliminary. The mixing ratio of CO₂ in dry air varied between 374.5 and 378.5 $\mu\text{mol mol}^{-1}$ throughout the cruise. The range of the values may decrease once the values affected by the ship's exhaust gases have been removed. Atmospheric pCO₂ ranged from 365 to 379 μatm . This variation resulted from changes in atmospheric pressure between 985 and 1025 mbar.

Surface water pCO₂ varied from 290 to 400 μatm in the Crozet area (Fig. 6.2). Large areas, in particular to the north of the Crozet plateau, were sinks for atmospheric CO₂. Areas with strong algal blooms had low pCO₂ and high oxygen saturation (Fig. 6.2). Such areas were encountered at M4 (15493), during the first SeaSoar survey (SS15519), and at M9 (15544). These areas of high biological activity are also evident from other surface water parameters, such as chlorophyll, Fv/Fm (Mark Moore, personal communication) and satellite images of ocean colour (Hugh Venebles and Raymond Pollard, personal communication).

Small to moderate sources for atmospheric CO₂ were found south of the plateau, in the Canal des Orgues between the Ile de la Possession and Ile de l'Est, and at station M3. The highest values were found at station M3 (15494/495/498/518), in the Canal des Orgues, at the 3000 m contour south of the straits, and at station M2 (15504). The supersaturation of pCO₂ may reflect seasonal warming of the water in areas with low marine productivity. The highest values may also reflect some input from deeper water rich in CO₂, especially as most of these sites, except for M2 are in locations where the topography of the plateau might affect the movement of the water.

Future work

- *The importance of natural iron fertilisation from shallow topography for the marine CO₂ sink near the Crozet Plateau* - Comparison of surface water pCO₂ and O₂ with other underway parameters, such as the concentrations of nutrients, chlorophyll, and iron, as well as with satellite observations of ocean colour and sea surface temperature will illustrate the spatial and temporal evolution of the Crozet blooms. The vertical profiles of DIC and alkalinity may allow testing whether any deeper water has reached the surface at the stations close to the plateau. Combination of the CO₂ data with the iron data (Peter Statham, Florence Nadelec, H el ene Planquette) will provide information on the factors controlling the oceanic CO₂ sink and whether natural iron fertilisation from shallow topography plays an important role.

This objective will also include study of CO₂ data previously collected in the Crozet area by OISO (Oc ean Indien Service d'Observation) scientists. This work will be carried out in collaboration with Nicolas Metzl and Alain Poisson (Laboratoire de Biog eochimie et Chimie Marines, Universit e Jussieu, Paris). The OISO program continues a valuable time series (since 1984) of surface water CO₂ measurements in the Indian sector of the Southern Ocean. It is jointly funded by INSU (Institut National des Sciences de l'Univers), IPEV (Institut Polaire Fran ais Paul Emile Victor) and IPSL (Institut Pierre Simon Laplace).

- *A carbon budget for the Crozet blooms* - The vertical profiles of DIC will allow calculation of the deficit in dissolved inorganic carbon in the mixed layer. The organic and inorganic carbon stocks and rates of change in the stocks will be combined into a comprehensive carbon budget for the blooms in collaboration with other cruise participants.
- *Effects of natural and anthropogenic iron fertilisation on oceanic CO₂ uptake* - Comparison of changes in fCO₂ and DIC in the Crozet blooms to results from algal blooms near the Polar Front, in SOIREE, and in EisenEx (Bakker et al., 1997, 2001, 2005) will allow testing whether natural and anthropogenic iron fertilisation affect CO₂ air-sea exchange and carbon cycling in similar ways.
- *Potential applications of satellite observations for quantifying oceanic CO₂ uptake* - The research will investigate potential uses of satellite information for quantifying CO₂ air-sea transfer, following an approach similar to Boutin et al. (1999). We will also compare how oceanic CO₂ uptake and carbon export compare with satellite based estimates of primary productivity and with Schlitzer's POC export (2002) for this region. This research is closely related to CASIX (Centre for Observation of Air-Sea Interactions and Fluxes; <http://www.pml.ac.uk/casix/>).
- *CO₂ air-sea transfer between the Crozet plateau and South Africa* - Surface water fCO₂ measurements will be made during the repeat transects between the Crozet Plateau and South Africa. The data will provide insight into the variation of CO₂ air-sea exchange between the plateau and South Africa from November to January.
- *Quantification of the air-sea gas transfer velocity* - The CO₂ air-sea flux will be calculated from the CO₂ air-sea concentration difference and wind speed. These indirect CO₂ air-sea fluxes will be compared to CO₂ fluxes, which have been measured by the eddy correlation method throughout the cruise (Robin Pascal, Margaret Yelland). The comparison will hopefully allow independent quantification of the gas transfer velocity for various wind speed regimes during the cruise. The oxygen excess (Richard Sanders)

and CO₂ deficit in surface waters will be compared in order to assess if it is possible to calculate an average gas transfer velocity for the period preceding the measurements.

This future work will be carried out in close collaboration with other cruise participants, who are not always mentioned individually in the above text. The collaborative effort will hopefully be reflected in several multi-author research articles. In some cases other participants may lead the research.

References

- Aanderaa (2003) TD 218 Operating manual oxygen optode 3830 and 3930. 9th edition. Aanderaa Instruments AS, Bergen, Norway, 44 pp.
- Baar, H.J.W. de, J.T.M. de Jong, D.C.E. Bakker, B.M. Löscher, C. Veth, et al. (1995) Importance of iron for plankton blooms and carbon dioxide drawdown in the Southern Ocean. *Nature* 373, 412-415.
- Bakker, D.C.E., H.J.W. de Baar, U.V. Bathmann (1997) Changes of carbon dioxide in surface waters during spring in the Southern Ocean. *Deep Sea Research II* 44, 91-128.
- Bakker, D.C.E., A.J. Watson, C.S. Law (2001) Southern Ocean iron enrichment promotes inorganic carbon drawdown. *Deep-Sea Research II* 48, 2483-2507.
- Bakker, D.C.E., Y. Bozec, P.D. Nightingale, L. Goldson, M.-J. Messias, H.J.W. de Baar, M.I. Liddicoat, I. Skjelvan, V. Strass, A.J. Watson (2005) Iron, dispersion, and mixing affect biological carbon uptake in two Southern Ocean iron fertilisation experiments, SOIREE and EisenEx. *Deep-Sea Research I*, accepted.
- Boutin, J., J. Etcheto, Y. Dandonneau, D.C.E. Bakker, R.A. Feely, et al. (1999) Satellite sea surface temperature: a powerful tool for interpreting in situ pCO₂ measurements in the equatorial Pacific Ocean. *Tellus* 51B, 490-508.
- Caldeira, K., P.B. Duffy (2000) The role of the Southern Ocean in uptake and storage of anthropogenic carbon dioxide. *Science* 287, 620-622.
- CAVASSOO (2004) Final report of the EU CAVASSOO project (CARbon Variability Studies by Ships Of Opportunity, EVK2-CT-2000-00088).
- DOE (1994) Handbook of methods for the analysis of the various parameters of the carbon system in sea water; version 2. Dickson, A.G., C. Goyet (Eds.). ORNL/CDIAC 74.
- ETOPO 5 (1988) Digital relief of the surface of the earth. Data Announcement 88-MGG-02. National Oceanographic and Atmospheric Administration, National Geophysical Data Center, Boulder, Colorado, USA.
- Garcia, H.E., L.I. Gordon (1992) Oxygen solubility in seawater: Better fitting equations. *Limnology and Oceanography* 37, 1307-1312.
- Johnson, K.M., K.D. Wills, D.B. Butler, W.K. Johnson, C.S. Wong (1993) The performance of an automated continuous gas extractor and coulometric detector. *Marine Chemistry* 44, 167-188.
- Matear, R.J., A.C. Hirst (1999) Climate change feedback on the future oceanic CO₂ uptake. *Tellus* 51B, 722-733.
- Mintrop, L. (2004) VINDTA, Versatile Instrument for the Determination of Titration Alkalinity. Manual for versions 3S and 3C. Version 2.0. MARine ANalytics and DATA (MARIANDA), Kiel, Germany, 45 pp.
- Nielsdóttir, M. (2004) Carbon variability studies: A study of the air-sea exchange with an oxygen optode. MSc thesis. Technical University of Denmark, DTU, Kgs. Lyngby, Denmark.
- Prentice, I.C., G.D. Farquhar, M.J.R. Fasham, M.L. Goulden, M. Heimann, et al. (2001) The carbon cycle and atmospheric carbon dioxide. 183-237. In J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, et al. (eds.) *Climate change 2001: The scientific basis. Contribution of WG I to the IPCC Third Assessment Report*. Cambridge University Press, Cambridge.

- Rayner, P.J., I.G. Enting, R.J. Francey, R. Langenfelds (1999) Reconstructing the recent carbon cycle from atmospheric CO₂, δ¹³C and O₂/N₂ observations. *Tellus* 51B, 213-232.
- Sarmiento, J.L., T.M.C. Hughes, R.J. Stouffer, S. Manabe (1998) Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature* 393, 245-249.
- Sarmiento, J.L., P. Monfray, E. Maier-Reimer, O. Aumont, R.J. Murnane, J.C. Orr (2000) Sea-air fluxes and carbon transport: A comparison of three ocean general circulation models. *Global Biogeochemical Cycles* 14, 1267-1281.
- Schlitzer, R. (2002) Carbon export fluxes in the Southern Ocean: results from inverse modelling and comparison with satellite-based estimates. *Deep Sea Research II* 49, 1623-1644.
- Sloyan, B.M., S.R. Rintoul (2001) Circulation, renewal and modification of Antarctic Mode and Intermediate Water. *Journal of Physical Oceanography* 31, 1005-1030.
- Smith W.H.F., D.T. Sandwell (1997) Global seafloor topography from satellite altimetry and ship depth soundings. *Science* 277, 1956-1962.
- Takahashi, T., J. Olafsson, J.G. Goddard, D.W. Chipman, S.C. Sutherland (1993) Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochemical Cycles* 7, 843-878.
- Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, et al. (2002) Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects. *Deep Sea Research II* 49, 1601-1622.

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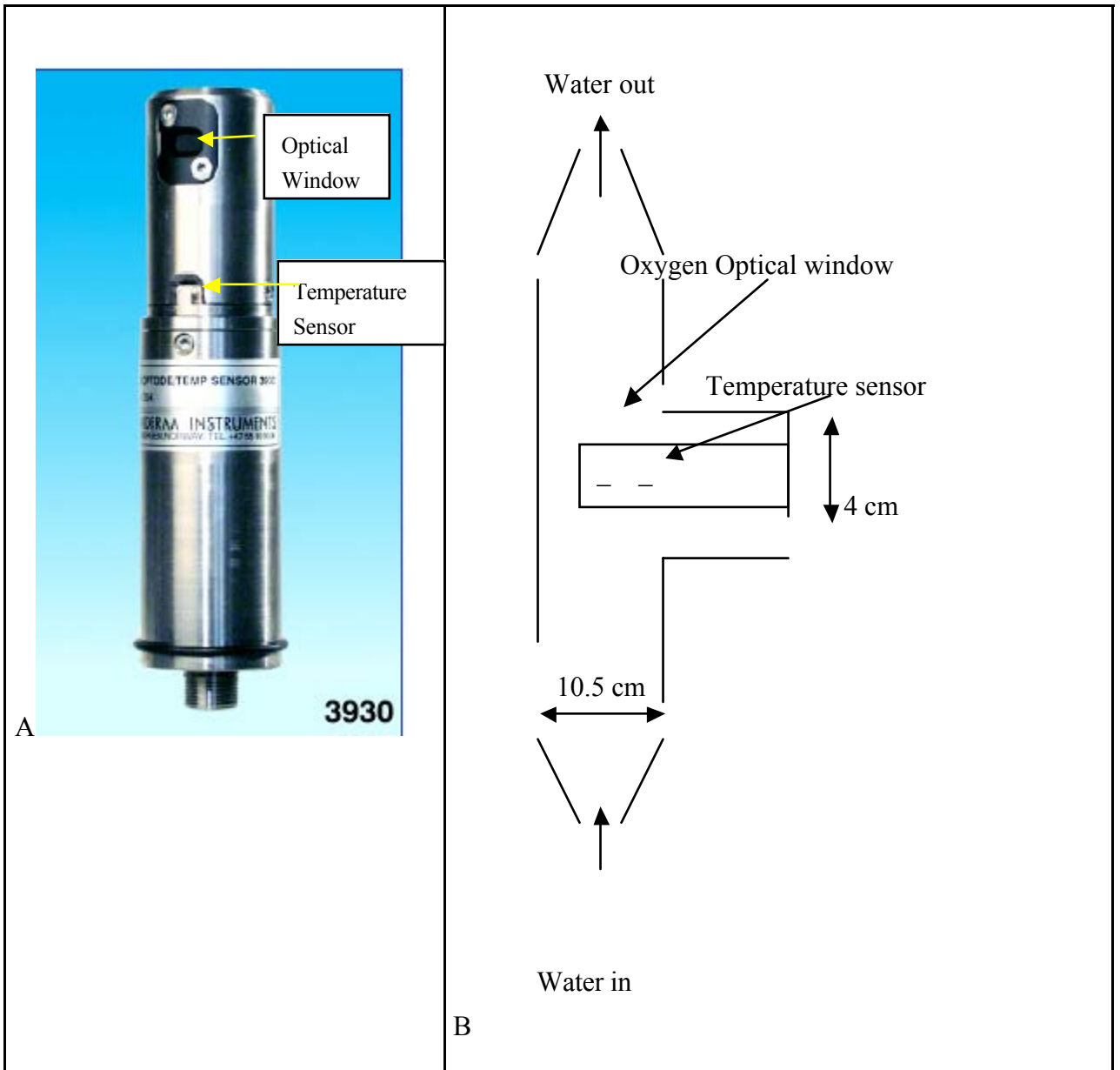


Fig. 6.1 (a) The optode 3930 (Aanderaa, 2003) and (b) the purpose built housing for the optode (Nielsdóttir, 2004)

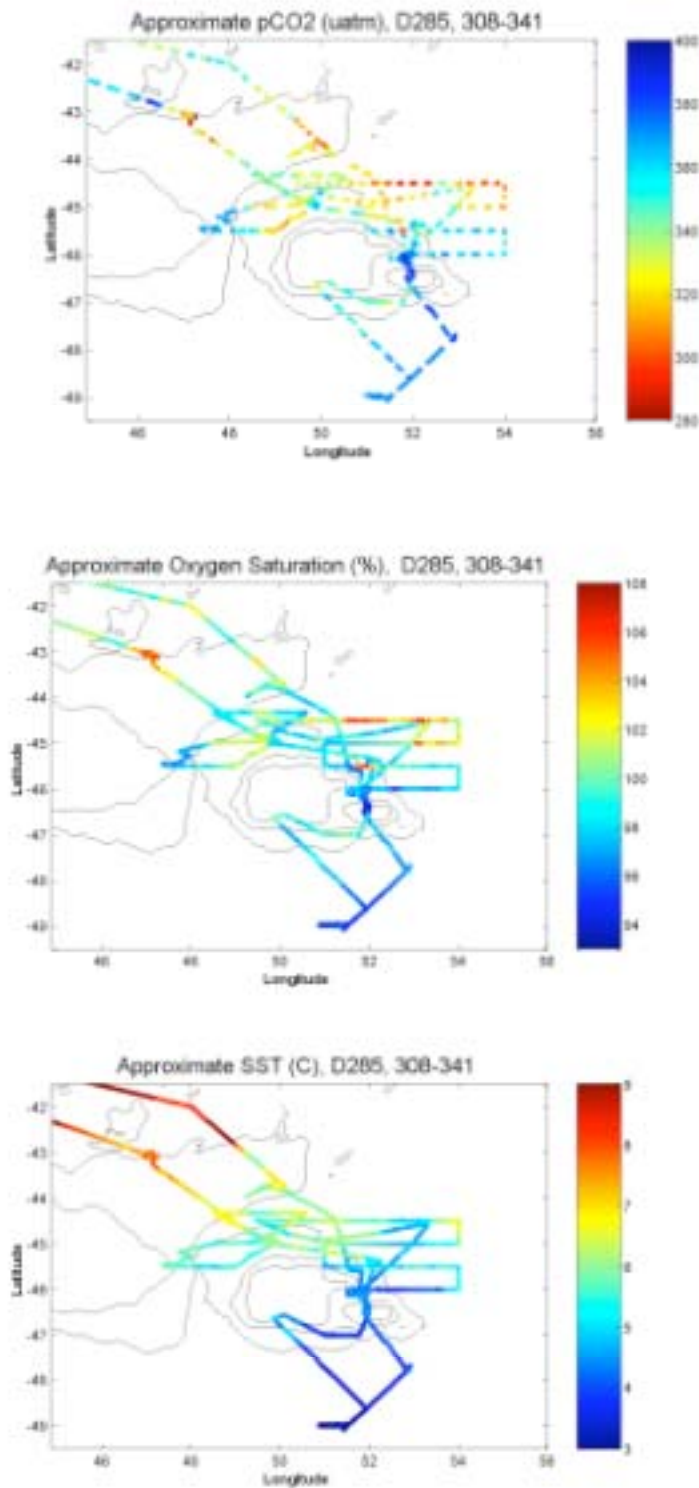


Fig. 6.2 The spatial distribution of (a) surface water pCO₂ (µatm), (b) the percentage oxygen saturation, and (c) the approximate sea surface temperature (°C) for the Crozet area. The colour scale of surface water pCO₂ has been reversed, such that high oxygen saturation and low pCO₂ both show as a red colour. Depth contours of 1000 m, 2000 m, and 3000 m are shown (ETOPO 5, 1988). A better topography is now available for the area (Smith and Sandwell, 1997). The approximate sea surface temperature was calculated by subtraction of 0.4°C from the temperature in the equilibrator.

6.2 Leg 2 D286

Methods

Underway parameters: oxygen and pCO₂

The partial pressure of CO₂ (pCO₂) in surface water and marine air, and the oxygen concentration of surface water were determined in a similar manner to the first leg. A bad electrical connection resulted in a valve failure on the online pCO₂ instrument on 19 December 2004. Support from Dougal Mountiford and Jeff Bicknell (UKORS) kept the downtime of the instrument to a minimum (2-3 hours). A roll of the ship sent the online pCO₂ instrument flying on 16 January 2005. Fortunately the instrument seems to have suffered only minor damage. In future the instrument needs better securing. Preliminary pCO₂ and oxygen data are available for the cruise until 14 January.

Vertical profiles of DIC and alkalinity

Samples for the analysis of dissolved inorganic carbon (DIC) and alkalinity were taken from the CTD at 25 stations. Typical sampling depths were: 10, 20, 40, 60, 80, 100, 150, 200, 300, 400, and 500 m. Repeat stations were carried out at M9 (leg 1+2), M10 (leg 2), M2 (leg 1+2), M3 (leg 1+2), M6 (leg 1+2), and the bloom site near M3 (leg 2). The CTD section between M3 and M5 was sampled. In total 261 CTD samples were analysed for DIC and alkalinity. All samples were analysed within 8 days of collection.

The analysis of DIC and alkalinity was carried out in a similar fashion to the previous leg (D285). Certified Reference Material (batch 66) was used to calibrate the DIC and alkalinity data. At least three replicate analyses were made on each DIC sample, until two replicates were within 1 $\mu\text{mol carbon kg}^{-1}$ (100 counts) for a blank below 0.3 $\mu\text{mol carbon kg}^{-1} \text{ min}^{-1}$ (30 counts min^{-1}). The analysis of DIC suffered from similar problems as during the previous leg with a high initial instrument blank for new coulometer cells. The blank problem may have originated from a variable quality of the MilliQ water, which was used for cell cleaning. The DIC data have an estimated precision and an accuracy better than 2.7 $\mu\text{mol kg}^{-1}$ after Bakker et al. (2001). Two or three replicates were run on each alkalinity sample, until the difference between two replicates was less than 1 $\mu\text{mol kg}^{-1}$. Processing of the DIC and alkalinity data is in progress.

Results

Surface water pCO₂ values ranged from 340 to 370 μatm to the north, east, and south of the plateau with occasionally higher values of 380 μatm (Fig. 6.3). Atmospheric pCO₂ was close to 373 μatm (+/-5 μatm). This made the Crozet area a significant sink for atmospheric CO₂.

In comparison with leg 1 (D285) the signature of strong algal blooms north of the plateau had disappeared in surface pCO₂ and O₂ by late December (Fig. 6.3). The bloom north of Ile de la Possession and Ile de l'Est (46°09'S 51°51'E) in early January was a notable exception to this. In this bloom pCO₂ was as low 300 μatm , while the oxygen saturation was up to 108% (Figs 6.4 and 6.5).

South of the plateau surface water pCO₂ had decreased by about 15 μatm between late November (D285) and the first days of January. This pCO₂ decrease occurred despite warming of the surface water by about 1°C. This suggests that biological carbon uptake promoted a pCO₂ reduction of 30 μatm .

Relatively high surface water $p\text{CO}_2$ values of $380 \mu\text{atm}$ were encountered on the Crozet plateau at depths shallower than a 1000 m, for example in the Baie aux Americains (Ile de la Possession) on 22 December 2004, and in the Baie du Marin (Ile de la Possession) on 8 January 2005. Such relatively high $p\text{CO}_2$ values were also encountered over the plateau during D285 and during certain French Minerve and OISO cruises (data by Alain Poisson and Nicolas Metzl, LOCEAN, Paris). A $p\text{CO}_2$ maximum, an oxygen minimum, and a minimum of sea surface temperature (SST) coincided with a shallowing of the isotherms by 50 m at the shallowest point (~ 150 m deep) of the Canal des Orques, the Strait between Ile de la Possession and Ile de l'Est, in the SeaSoar survey on 31 December 2004. A $p\text{CO}_2$ maximum, an oxygen minimum and a distinct SST minimum also occurred at $46^\circ 17' \text{S}$ $51^\circ 42' \text{E}$, immediately north of Ile de la Possession on 10 and 12 January 2005. It will be interesting whether the parallel SeaSoar survey on 12 January showed a shallowing of the isotherms. The results of the first SeaSoar survey suggest that vertical advection may explain some of the relatively high surface $p\text{CO}_2$ values over the plateau.

A salinity minimum (fresh by 0.03 units) was apparent between $51^\circ 47' \text{E}$ and $51^\circ 58' \text{E}$ in the CTD section along $46^\circ 17' \text{S}$, just east of the aforementioned $p\text{CO}_2$ maximum. Surface water $p\text{CO}_2$ of $\sim 355 \mu\text{atm}$ was relatively low in the salinity minimum, while the oxygen saturation was relatively high. Further study is necessary to assess how surface water $p\text{CO}_2$ varied with salinity in the vicinity of the islands.

Conclusion

The Crozex cruises (D285, D286) have provided a wealth of data on the evolution of the carbonate system from spring to summer in the Crozet area. The importance of iron fertilisation from the Crozet plateau for algal growth and marine carbon cycling will be assessed from the iron, radium, chlorophyll, $p\text{CO}_2$, and O_2 data. Careful study of the inorganic carbon results from both legs will highlight the processes controlling surface $p\text{CO}_2$ and the vertical distribution of DIC and alkalinity in the area, notably biological processes (algal carbon uptake, remineralisation, carbon export), seasonal warming, vertical advection, air-sea gas transfer, and possibly freshwater input. Changes in the vertical profiles of DIC and alkalinity at repeat CTD stations will allow quantification of net community production. Combination of the surface data with satellite observations of ocean colour and sea surface temperature will place the shipboard $p\text{CO}_2$ data in a wider context and may possibly allow the extrapolation of the surface water $p\text{CO}_2$ data for well mapped areas (eg. SeaSoar surveys), by a method such as co-Kriging. This work will be pursued in the context of the NERC CASIX and BICEP programs, in collaboration with researchers of the French OISO program.

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References

- Bakker, D.C.E., A.J. Watson, C.S. Law (2001) Southern Ocean iron enrichment promotes inorganic carbon drawdown. *Deep-Sea Research II* 48, 2483-2507.
- ETOPO 5 (1988) Digital relief of the surface of the earth. Data Announcement 88-MGG-02. National Oceanographic and Atmospheric Administration, National Geophysical Data Center, Boulder, Colorado, USA.
- Smith W.H.F., D.T. Sandwell (1997) Global seafloor topography from satellite altimetry and ship depth soundings. *Science* 277, 1956-1962.

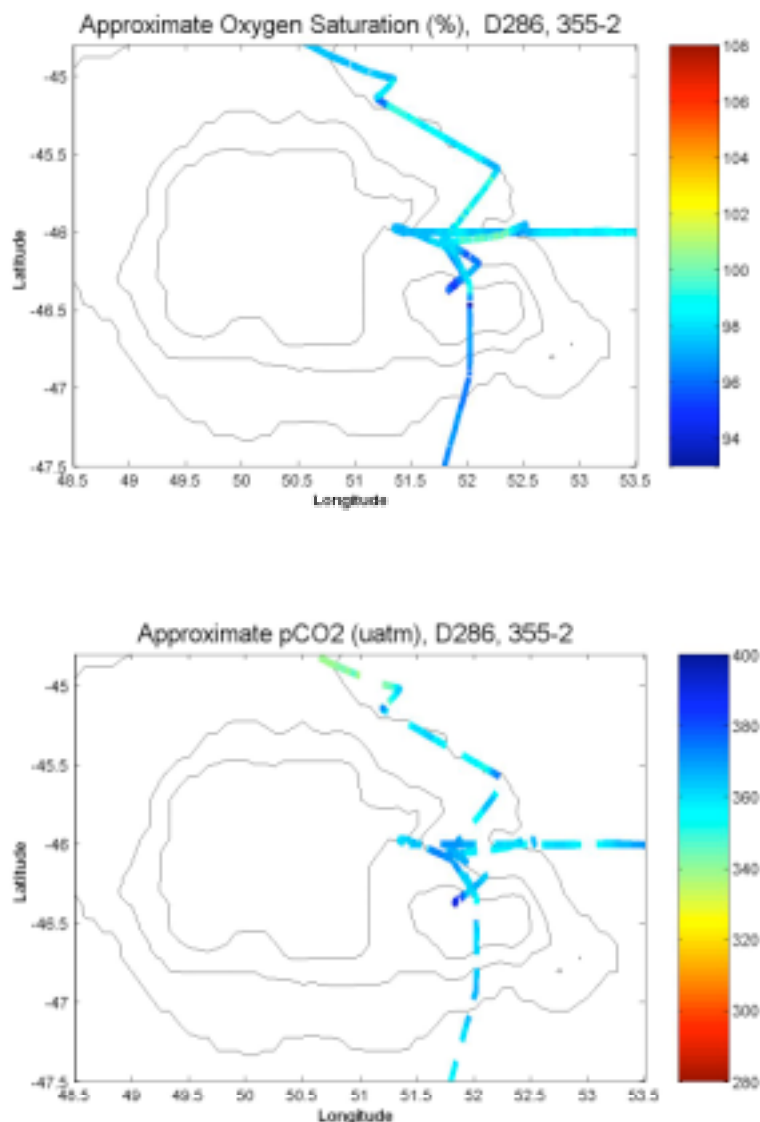


Fig. 6.3 The spatial distribution of surface $p\text{CO}_2$ and O_2 in the vicinity of the Crozet plateau from 21 December 2004 to 2 January 2005. The colour scale of surface water $p\text{CO}_2$ has been reversed, such that high oxygen saturation and low $p\text{CO}_2$ both have a red colour. Depth contours of 1000 m, 2000 m, and 3000 m are shown (ETOPO 5, 1988). A better topography is now available for the area (Smith and Sandwell, 1997).

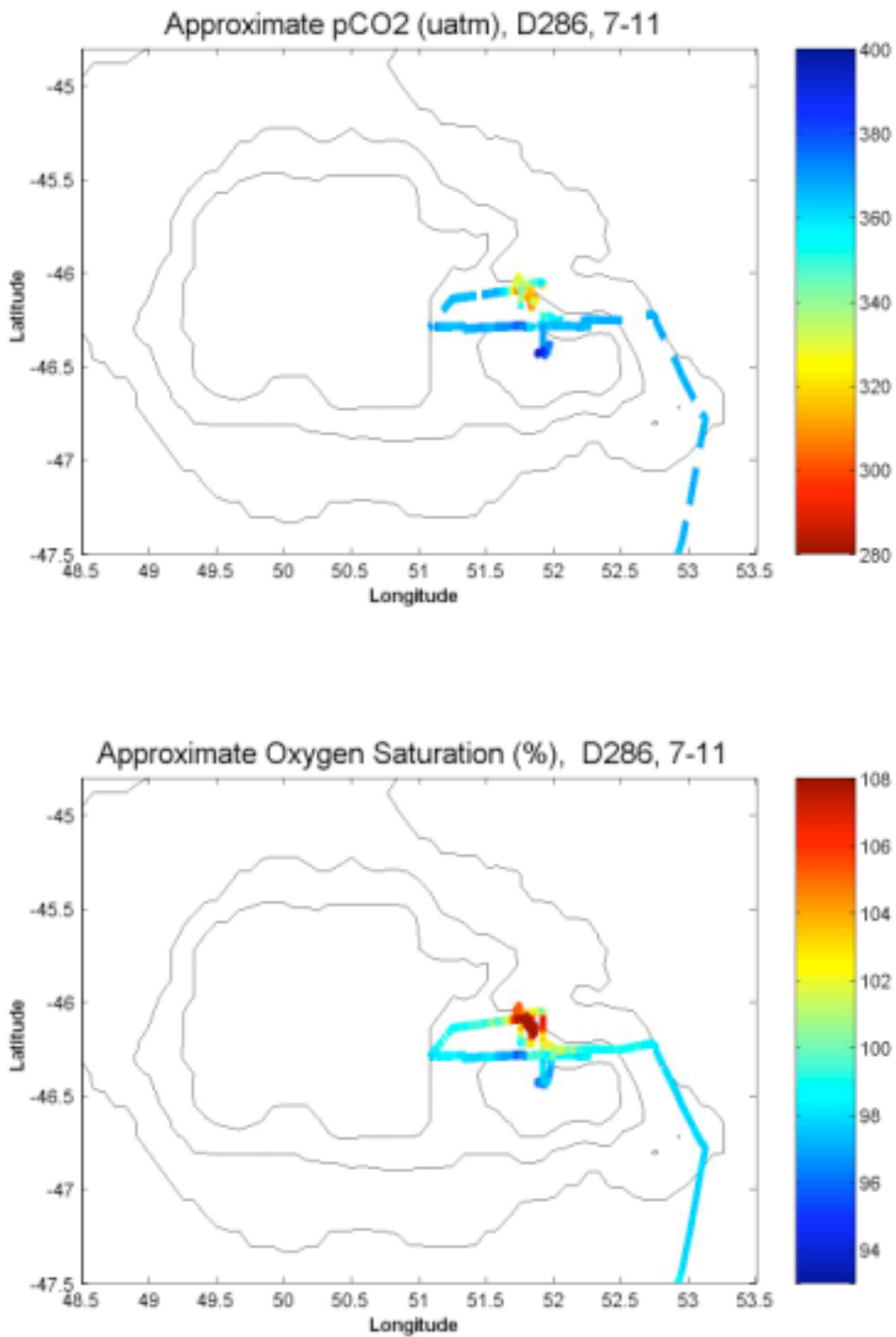


Fig. 6.4 The spatial distribution of surface pCO₂ and O₂ in the vicinity of the Crozet plateau from 7 to 11 January 2005. Depth contours are shown at 1000 m intervals (ETOPO 5, 1988).

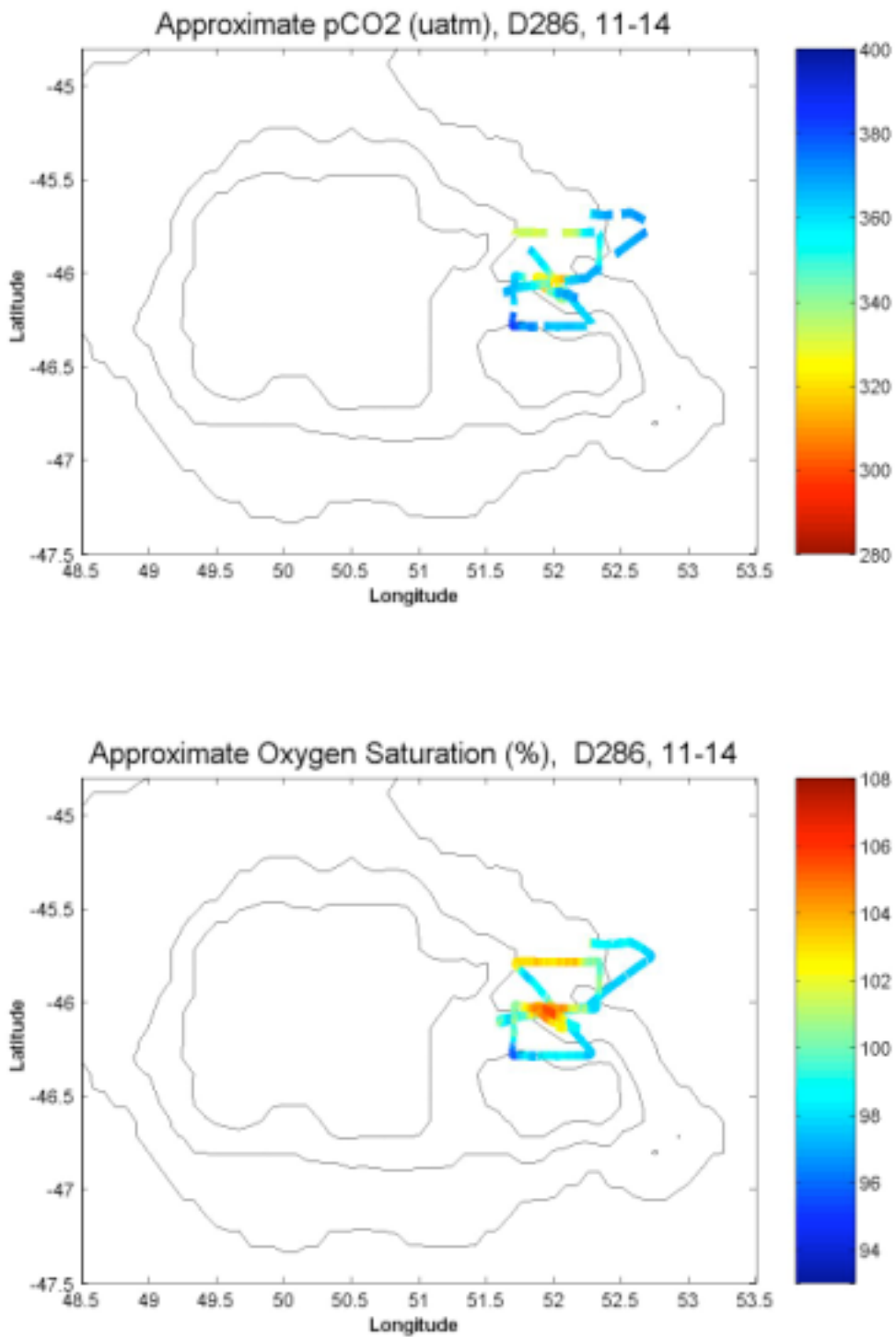


Fig. 6.5 The spatial distribution of surface pCO₂ and O₂ in the vicinity of the Crozet plateau from 11 to 14 January 2005. Depth contours of 1000 m, 2000 m, and 3000 m are shown (ETOPO 5, 1988).