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### Deep-Sea Research I

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# Distribution and ventilation of water masses in the western Ross Sea inferred from CFC measurements



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#### ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form
28 November 2014
Accepted 30 November 2014
Available online 10 December 2014

Keywords: CFCs Antarctic surface waters Antarctic bottom water Ross Sea ventilation

#### ABSTRACT

During the CLIMA Project (R.V. Italica cruise PNRA XVI, January–February 2001), hydrographic and chlorofluorocarbons (CFCs) observations were obtained, particularly in the western Ross Sea. Their distribution demonstrated water mass structure and ventilation processes in the investigated areas. In the surface waters (AASW) the CFC saturation levels varied spatially: CFCs were undersaturated in all the areas (range from 80 to 90%), with the exception of few stations sampled near Ross Island. In particular, the Terra Nova Bay polynya, where high salinity shelf water (HSSW) is produced, was a low-saturated surface area (74%) with respect to CFCs. Throughout most of the shelf area, the presence of modified circumpolar deep water (MCDW) was reflected in a mid-depth CFC concentration minima. Beneath the MCDW, CFC concentrations generally increased in the shelf waters towards the seafloor. We estimated that the corresponding CFCs saturation level in the source water region for HSSW was about 68–70%. Waters with high CFC concentrations were detected in the western Ross Sea on the down slope side of the Drygalski Trough, indicating that AABW was being supplied to the deep Antarctic Basin.

Estimates of ventilation ages depend strongly on the saturation levels. We calculated ventilation ages using the saturation level calibrated tracer ratio, CFC11/CFC12. We deduced a mean residence time of the shelf waters of about 6–7 years between the western Ross Sea source and the shelf break.

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#### 1. Introduction

The formation of dense waters at high latitudes and the subsequent sinking and spreading of the water in the abyssal ocean are integral parts of the global ocean's overturning circulation. This overturning circulation has profound effects on the heat budget of the Earth and impacts the regional and global climate. Apart from heat, the sinking waters also carry dissolved constituents, such as dissolved oxygen (O<sub>2</sub>), nutrients and carbon dioxide (CO<sub>2</sub>), and the strength of the overturning circulation ultimately determines the oxygen, nutrient, and carbon levels in the abyss (Schlitzer, 2007).

Southern overturning starts with the sinking of near-freezing water with temperatures of about  $-1.9\,^{\circ}\mathrm{C}$  in the shelf seas around Antarctica. This process occurs mainly in four locations, that is, in the Weddell Sea, Prydz Bay, Adélie Land and the Ross Sea (Orsi et al., 1999). Two shelf water masses (SW) of the Ross Sea are mainly involved in the formation of Antarctic bottom water (AABW): the high salinity shelf water (HSSW), characterized by

salinities between 34.75 and 34.85, and the deep ice shelf water (DISW), defined by temperatures below the freezing point at the sea surface (Jacobs et al., 1985). HSSW is formed mainly in the Terra Nova Bay (TNB) area during the austral winter (Budillon et al., 2003) and spreads northwards following the axis of the Drygalski Trough toward the shelf break off Cape Adare.

The most voluminous water mass in the Southern Ocean is the circumpolar deep water (CDW) carried eastward by the Antarctic circumpolar current (ACC). CDW is identified as a thick, salty and oxygen-poor layer rising from the mid-depths of the subtropical regime. Some CDW continues poleward and enters the cyclonic Ross Gyre, where it is stratified between the much colder Antarctic surface water (AASW) above and Antarctic bottom water below (Orsi and Wiederwohl, 2009). There are large vertical displacements of water parcels over the water column within and south of the ACC, with deep water moving poleward and upper ocean water equatorward. This shallow meridional circulation or upper cell (Speer et al., 2000) is linked to dynamical processes in the upper ocean; mesoscale eddies can also bring mass and other properties poleward and upward along isopycnal surfaces. The cyclonic circulation of the Ross Gyre can carry CDW poleward and waters influenced by the Ross Sea northward, mixing water

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masses and acting as a mechanism for horizontal transports of heat and freshwater. A westward current above the continental slope and shelf break of the Ross Sea is well developed and several poleward intrusions of CDW over the shelf have been detected corresponding to the location of the major banks that characterize the bottom topography.

Much of our knowledge about deep ocean circulation on both regional and large scales comes from inferences made on the basis of distributions of hydrographic parameters, such as temperature, salinity, O<sub>2</sub>, nutrients and chlorofluorocarbons (CFCs) (Schlitzer, 2007). The CFCs are synthetic halogenated methanes. The chemical structures of the CFCs used for ocean sciences are CCl<sub>3</sub> F for CFC-11, CCl<sub>2</sub>F<sub>2</sub> for CFC-12, and CCl<sub>2</sub>FCClF<sub>2</sub> for CFC-113 (Fine, 2011). They enter the ocean by gas exchange across the ocean-atmosphere interface and, compared to O2, they have the advantage of being chemically inert. Another advantage of using CFCs compared to other tracers is their transient nature, which allows deduction of advection rates and transit times as it has been done in the Weddell Sea (for example, Huhn et al., 2008, 2013). Hence, this suite of tracers is an excellent tool to understand the formation and spreading of water masses, to quantify their fraction as they mix, and to evaluate the age and the transit time distribution over the time period their input function is sufficiently well known. Since in the Ross Sea, sea ice apparently has a strong influence on the gas exchange, we have to consider how the saturation of CFCs changes over time (Rodehacke et al., 2010).

This study is based on CFC data collected in the western Ross Sea during the austral summer 2000–2001 within the XVI Antarctic Expedition of the Italian National Research Program in Antarctica (Programma Nazionale di Ricerca in Antartide, PNRA). Detailed investigations, focused on the mixing of the overflowing shelf waters and the entrained lower layers of CDW, were carried out by the CLIMA (climatic long term interaction for the massbalance in Antarctica) project across the shelf break. This work aims to examine the distribution of tracers in surface water of the western Ross Sea and to evaluate the ventilation and the transit time of SW on the continental shelf, extending a previous paper showing preliminary results (Rivaro et al., 2004).

#### 2. Materials and methods

#### 2.1. Sampling

CFC and O2 data were collected on board the R.V. Italica during the XVI PNRA-CLIMA Project survey (16th January-15th February 2001). The position of the casts is shown in Fig. 1. They were mainly in the western Ross Sea, along the Drygalski Trough from Terra Nova Bay polynya (TNBp) to the shelf break region off Cape Adare (CA); a few stations were also sampled both in the Glomar-Challenger Trough (GCT) and in the Ross Sea polynya (RSp). CTD (conductivity temperature depth) casts were performed using a Sea Bird Electronics SBE 9/11 probe with double temperature and conductivity sensors coupled to a carousel water sampler SBE 32. The CTD descent velocity was always below  $80 \text{ cm s}^{-1}$ . Calibration of temperature and conductivity sensors was performed at the SACLANT CENTRE of La Spezia (Italy) before and after the cruise. Hydrological data were corrected and processed according to international procedures (UNESCO, 1988). Standard algorithms (Fofonoff and Millard, 1983) were used to compute derived quantities such as potential temperature, salinity, and potential density anomaly. Water samples for chemical analyses were collected from 12-L Niskin bottles. The CFC samples were collected into 100-mL glass ampoules after flushing them with seawater for several ampoule volumes, and were flame-sealed under a flow of CFC-free N<sub>2</sub>. The amount of CFC degassing into the headspace was accounted for during the measurement procedure. The samples were stored under cold and dark conditions until the analysis.

#### 2.2. Chemical analyses

O<sub>2</sub> was measured on board using the Winkler method by automated micro-titrations (Grasshoff, 1983) with a potentiometric detection of the end point using a Methohm 719 titroprocessor. The measurement precision was  $\pm 0.05$  mg L<sup>-1</sup>. The CFC measurements, performed at Lamont-Doherty Earth Observatory (LDEO), Columbia University, Palisades, NY (USA), used a purge and trap sample system interfaced to a gas chromatograph (GC) with an electron capture detector (ECD) (Smethie et al., 2000). The precision of the measurement was the greater of 1.5% or 0.04 pmol  $kg^{-1}$  for CFC-11 and 1.5% or 0.03 pmol kg<sup>-1</sup> for CFC-12. Calibration was done using synthetic air, prepared from ultra-pure O<sub>2</sub> and N<sub>2</sub>, containing known amounts of CFC-11, CFC-12 and CFC-113. The detection limit was  $0.01 \text{ pmol kg}^{-1}$  for all three CFCs. For comparison with the atmospheric source, the CFC concentrations are converted to partial pressure (ppt, parts per trillion) using the solubility function of Warner and Weiss (1985). For the southern hemisphere atmospheric time history, we used the values calibrated on SIO98 scale from http:// cdiac.ornl.gov/oceans/new\_atmCFC.html.

#### 2.3. Data processing

#### 2.3.1. Optimum multi parameter (OMP) analysis

The optimum multi parameter (OMP) analysis (Tomczak and Large, 1989) was used to calculate the source water distributions as a fraction of the total water mixture at the stations in the section 11-65 compiled along the Drygalski Through, from TNBp to the slope area off CA (cf. Fig. 1). In our study we have applied the extended OMP, because a higher number of variables (in our case  $\theta$ , salinity, O<sub>2</sub> and CFCs) allowed resolution of the mixing system for more than two source water types. The most important step in this analysis is to express all seawater samples as linear combinations of some selected sea water types (SWTs), whose physical and chemical properties are fully known (Poole and Tomczak, 1999). Following a similar study performed by Rivaro et al. (2010) for the same area, we considered the four SWTs of the investigated area to be AASW, HSSW, CDW and AABW. The characteristics of the selected water masses are reported in Section 3. We define the AASW, CDW, HSSW and AABW within limits of temperature, salinity, and density and we calculate means and standard deviations of their properties from our available observations, using data that coincide with the data under consideration (cf. Table 1). The OMP analysis we carried out assumes that the variable properties for the SWTs are conservative. Three of the properties used, CFC-11, CFC-12 and oxygen, are not normally conservative; the input of CFC-11 and -12, and hence end member concentrations, change with time, and oxygen is produced and consumed by photosynthesis and respiration, respectively. However, in the situation described here, these properties are essentially conservative for the mixing and advection time scales of the STW end members. Basically mixing is occurring between very young water (the shelf water masses) and very old water (CDW) to form AABW. A number of studies, including this one, have indicated that the shelf water masses are no older than 6-7 years. The CFC-11 and CFC-12 concentrations in the atmosphere have changed little since 1994, which is 7 years prior to the observations reported here. We considered the atmospheric concentration from 1994 to 2000 and the corresponding equilibrium concentration calculated at  $\vartheta$ =0.00 °C and S=33.8. The CFC-11 equilibrium concentration ranges from 7.03 to  $6.96\,\mathrm{pM\,kg^{-1}}$  and the CFC-12 from 3.31 to  $3.51 \text{ pM kg}^{-1}$ , respectively. Thus, the variability due to the change in atmospheric concentration is lower than the larger

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