

## Review of CHINARE chemical oceanographic research in the Southern Ocean during 1984–2016

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**Abstract** Between 1984 and 2016, China executed 33 Antarctic cruises with the icebreaker R/V *Xuelong*, which have provided opportunities for Chinese scientists to investigate the status and changes of the Southern Ocean. Research in chemical oceanography constitutes one of the primary missions of the Chinese National Antarctic Research Expedition (CHINARE). This paper reviews nearly 30 years of Chinese Antarctic expeditions, focusing on the major progress achieved in chemical oceanographic research. Specifically, the sea-surface distributions and air–sea fluxes of CO<sub>2</sub> and N<sub>2</sub>O are considered, and the transport, flux, and budget of organic matter are investigated based on isotopes in the Southern Ocean, especially in Prydz Bay. In addition, the nutrient distribution and deep-water particle export in Prydz Bay and the study of aerosol heavy metal characteristics are considered. Finally, the prospects for future Chinese Antarctic chemical oceanographic research are outlined.

**Keywords** chemical oceanography, Southern Ocean, CHINARE, Prydz Bay

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### 1 Introduction

The first Chinese National Antarctic Research Expedition (CHINARE-01) was in 1984. Vigorous progress in the expedition program has developed a new research area in chemical oceanography, a field in which remarkable progress has been achieved following 30 years' effort. This paper offers a brief introduction of the primary research areas, reviews the major achievements, and outlines the prospects for further study of chemical oceanography by China.

In the previous two decades, the Antarctic Ocean has experienced rapid climate-related changes, e.g., variation in

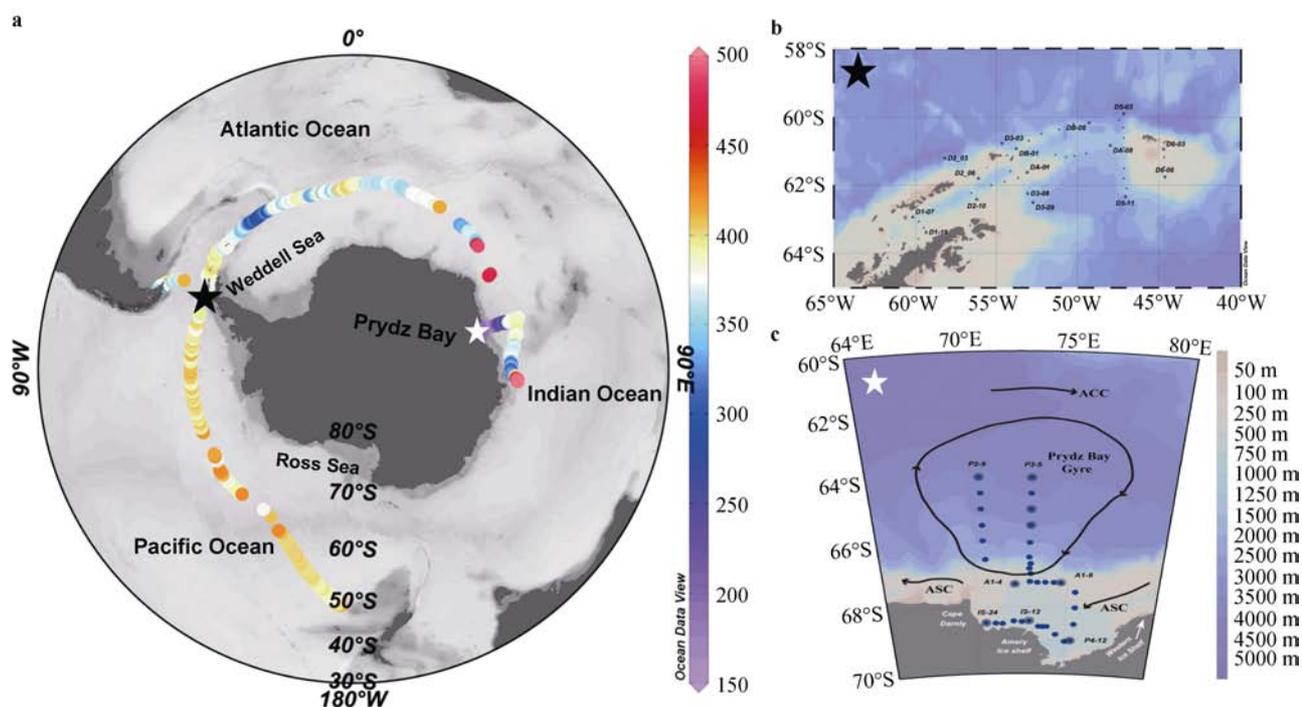
sea ice (Kurtz and Markus, 2012), increase in sea surface temperature (Frölicher et al., 2015), strengthened westward wind (Thompson and Solomon, 2003), and change in stratospheric ozone depletion (Turner et al., 2009). The use of isotopes and marine aerosol heavy metal characteristics to establish how the concentrations of nutrients, air–sea fluxes of CO<sub>2</sub>, N<sub>2</sub>O, and DMS (dimethyl sulfide), and the transport, flux, and budget of organic matter in the Southern Ocean might vary in response to the rapid environmental and climatological changes is therefore important for the scientific community and the public. However, because of limited numbers of *in situ* measurements and insufficient sampling, the status and related control mechanisms of chemical oceanographic responses to these environmental changes require further research. The CHINARE cruises

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(1984–2016) took place during this period of change, allowing scientific assessment of the biogeochemical responses to the rapid climatological changes in the area of the Antarctic Ocean. Many published papers have reported on the observations made during the CHINARE cruises during this period. These have increased the understanding of the biogeochemical processes occurring in the Antarctic Ocean, which will benefit international efforts both in comprehending the prevailing processes and in predicting their future changes. These papers provide an overview of the basic characteristics of the Antarctic Ocean, especially Prydz Bay, and all report on unique geographic locations that are highly suitable for biogeochemical observations and studies.

Here, we emphasize the study of both the sea-surface distributions and the air–sea fluxes of CO<sub>2</sub> and N<sub>2</sub>O in Prydz Bay and the Southern Ocean (Figures 1a, 1b, and 2),

and we discuss their interactions with sea ice condition (Zhan and Chen, 2009; Chen et al., 2011; Gao et al., 2012; Zhan et al., 2015; Xu et al., 2016). Furthermore, we investigate the transport, flux, and budget of organic matter using isotopes (Qiu et al., 2004; He et al., 2007; Yang et al., 2009; Zhang et al., 2014), and we examine the distribution of nutrients and particle export in Prydz Bay (Hu et al., 2006, 2008; Han et al., 2011; Sun et al., 2012, 2013; Sun, 2013; Zhang et al., 2014). In addition, we consider the distribution and chemical speciation of marine sulfur characteristics, together with the air–sea flux of DMS (Chen et al., 2012), and we discuss both a field study of aerosol heavy metal characteristics and a fertilization experiment conducted in the Southern Ocean (Gao et al., 2013). All the research reported here has provided data for better evaluation of the distribution and of the control mechanisms of biogeochemical parameters in the Antarctic region.



**Figure 1** Study area of the CHINARE cruises. **a**, The track of the R/V *Xuelong* and the underway measurements of  $p\text{CO}_{2\text{sw}}$  (unit:  $\mu\text{atm}$ ) in 2009 (data from Xu et al., 2009); **b**, the Antarctic Peninsula; **c**, Prydz Bay, revised from Figure in Zhan et al. (2015). Note: stars in (a) identify the locations of the areas shown in (b) and (c).

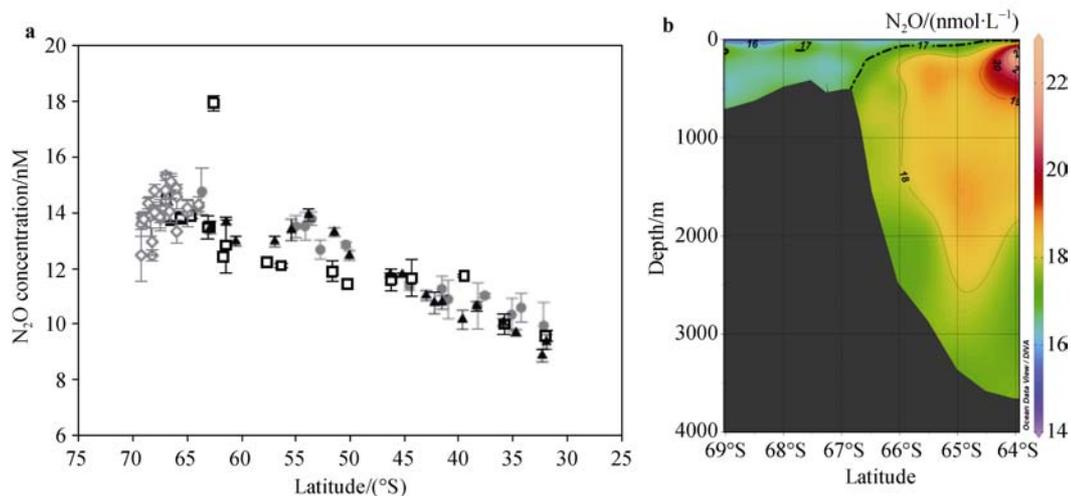
## 2 Nutrient distributions and particle export in Prydz Bay

### 2.1 Nutrients

Many studies on nutrients in Prydz Bay have shown the distributions of nitrate, phosphate, and silicate have similar characteristics, i.e., low values within the bay and high values outside (Hu et al., 2006; Han et al., 2011; Sun et al., 2012). Generally, the concentrations fall from coastal regions to offshore areas at latitudes of 67°–68°S. The decrease can be attributed to a combination of nutrient

consumption by phytoplankton and a lack of nutrient injection in coastal regions. However, it has been found that the distribution of ammonium salt is the opposite of nitrate, dropping from high values inside the bay to low values outside. In addition, the surface distribution of nitrite both inside and outside the bay is reasonably constant.

Sun et al. (2012) collected seawater samples from Prydz Bay during the Antarctic summer of 2011 and they analyzed the contents of Chl-*a* and other nutrients (i.e., nitrate, silicate, phosphate, and ammonium). They found the concentration of Chl-*a* in the surface water of Prydz Bay was highest at the margin of the ice shelf, lower at the



**Figure 2** a,  $N_2O$  concentration in surface seawater versus latitude along different legs of different cruise tracks and in Prydz Bay during CHINARE-22 (Zhan and Chen, 2009); b, profile distribution of  $N_2O$  during CHINARE-27 (Zhan et al., 2015). The location of the Antarctic Slope Front is shown as the dashed–dotted line.

continental shelf, and even lower on the continental slope and in the open sea. The vertical distribution of Chl-*a* is related to irradiation; thus, its content was found to be high in the upper waters and it decreased with depth. The horizontal and vertical distributions of phosphate, silicate, and nitrate were found to be the opposite of Chl-*a*, reflecting the increase in primary productivity due to sea ice melting. Furthermore, the enhancement of primary productivity was likely due to Fe supplies in Prydz Bay. Sun et al. (2012) found a chlorophyll maximum in the deep water along a section at 71 $^{\circ}E$ , which could be related to the supply of Fe at the maximum level, i.e., the water at the depth of the chlorophyll maximum might receive greater supply of Fe.

Sun et al. (2013) indicated the contents of dissolved Zn and Cd in the seawater of Prydz Bay were 1.04–5.60 and 0.069–0.696 nM (mean values: 3.39 and 0.273 nM), respectively. It has been established that the concentrations of dissolved Zn and Cd show little difference between Prydz Bay and the Weddell Sea, Scotia Sea, Ross Sea, and other continental seas of the South Atlantic Ocean (Abollino et al., 2001; Baars and Croot, 2011; Croot et al., 2011). However, they are considerably higher than found in Subantarctic waters (Ellwood et al., 2004, 2008). The content of Zn found in Subantarctic waters was very low, with a pM order of magnitude, which is considered “zinc confined”. In addition, the measured contents of dissolved Zn and Cd were lowest on the ice shelf, and the contents of trace elements on the continental shelf and in the deep sea were higher than on the ice shelf.

## 2.2 Particle export in Prydz Bay

According to Sun et al. (2013), the total material flux (TMF) of the Prydz Bay shelf area was 69747  $mg \cdot m^{-2} \cdot a^{-1}$  throughout the entire year, and the highest content of biogenic silica in the sediment was about 78.7% of the TMF,

similar to the annual TMF ratio of the 1000-m water layer in the Prydz Bay deep-sea area (Hu et al., 2006, 2008). This indicates that biological silicon was the continental and deep-sea sediments of Prydz Bay. Organic carbon and Al were the next most abundant elements, comprising about 4.6% and 0.8%, respectively, of the TMF in 2011. The content of biogenic silica and organic carbon in the raw material accounted for 83.3% of the TMF throughout the entire year of 2011, while <1.0% of Al represented the main source of rock-derived material, indicating that the content of bioparticulate matter in Prydz Bay largely determines the total annual particulate flux.

The TMF of the northern waters of Prydz Bay (62.47 $^{\circ}S$ , 72.98 $^{\circ}E$ ) in the 1000-m layer (water depth: 3980 m) from 1998 to 1999 was 13.00–334.59  $mg \cdot m^{-2} \cdot d^{-1}$  (Hu et al., 2006, 2008). This is markedly lower than that of the Prydz Bay shelf area, reflecting the biomass (Chl-*a*) of the phytoplankton in the deep sea and the shelf area of Prydz Bay. The Chl-*a* content of the Antarctic deep sea in summer from 1990 to 2002 was <0.3  $mg \cdot dm^{-3}$  (Zhang et al., 2014), while that at the M1 station of an intercropping area adjacent to the deep-sea area reached 3.95  $mg \cdot dm^{-3}$ , evidently higher than the deep-sea area. Sedimentation in Prydz Bay comprised mainly of bioparticulate matter, and the content of raw material (biological silicon, organic carbon, and calcium carbonate) was 51%–92%, of which biological silicon accounted for over 80% (Hu et al., 2006, 2008). The apparent phytoplankton content in the upper layer of the shelf area was obviously higher, resulting in the greater amount of bioparticulate matter captured in the lower layer of the water in comparison with the deep-sea area; thus, the TMF was clearly higher.

Sun et al. (2013) measured fluxes of particulate barium using time series sediment traps deployed at two stations on the continental shelf of Prydz Bay at depths of about 500 m from 7 December 2009 to 15 February 2010 and from 16

December 2010 to 16 December 2011. The annual fluxes were 12.3 and 18.4  $\text{mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$  for barium, and 8.9 and 14.9  $\text{mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$  for biogenic barium at the two stations. Based on the high preservation efficiency of biogenic barium and strong relationship between biogenic barium and organic carbon, Sun et al. (2013) suggested that biogenic barium could be considered a reliable proxy for marine export production. The calculated export productions were 6.9 and 14.9  $\text{g C}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$  at the two stations, based on a modified prediction equation that is more suitable for predicating export production for margin and shelf systems.

### 3 Distributions of CO<sub>2</sub> and its air–sea fluxes in the Antarctic

The Southern Ocean plays a crucial role both in the global carbon cycle and in climate change. A number of large-scale international cooperative projects, e.g., SO-JGOFS (Southern Ocean-Joint Global Ocean Flux Study), GLOCHANT (GLOBAL CHange and the ANTArctic), and SOIREE (Southern Ocean Iron Release Experiment), have been launched by various international organizations and countries to perform research on the carbon cycle in the Southern Ocean. China has also gradually developed a program to research the carbon cycle in the Southern Ocean. The relevant projects comprise the National Key Technology Research and Development Program of China during the 9th Five-Year Plan “Carbon Cycle in the Sea Ice Zone of the Southern Ocean”, National Key Technology Research and Development Program of the Ministry of Science and Technology of China during the 11th Five-Year Plan “Monitoring Technology and Application for Carbon Cycle in the Southern Ocean”, Chinese Polar Environment Comprehensive Investigation and Assessment Program during the 12th Five-Year Plan “Marine Chemistry and Carbon Flux in the Southern Ocean”.

The atmospheric and surface water CO<sub>2</sub> partial pressure has been studied as part of the CHINARE cruises since 1999. Onboard the ice-breaker R/V *Xuelong*, a carbon cycle laboratory was built, an underway *p*CO<sub>2</sub> system installed (the accuracy of the data was improved and ensured for the application of the CO<sub>2</sub>/H<sub>2</sub>O infrared analyzer Li-Cor 6262), and a special pumping line fitted to provide a continuous supply of surface water. To support the ongoing Sino–US carbon cycle projects, the carbon cycle laboratory onboard the R/V *Xuelong* was upgraded in 2007 with an improved surface water pumping system and an advanced underway *p*CO<sub>2</sub> system.

#### 3.1 Prydz Bay

Prydz Bay is the largest embayment on the broad east Antarctic continental shelf, lying offshore of the Amery Ice Shelf. The main flow of water inshore is along the coast from the West Ice Shelf, which maintains salinity in Prydz

Bay close to open ocean levels, i.e., 33.0–34.5 (Gibson and Trull, 1999). The seasonal temperature cycle of the surface waters is small, i.e., <2°C. Prydz Bay is an important area in the Southern Ocean and it plays an important role in the carbon cycle.

Gao et al. (2008) investigated the *p*CO<sub>2</sub> during the CHINARE-XVI cruises onboard the R/V *Xuelong* from November 1999 to April 2000. They found *p*CO<sub>2</sub> was low in the inshore areas of Prydz Bay but higher offshore. The observed distribution showed strong negative correlation with *Chl-a* concentration. This suggests that *p*CO<sub>2</sub> is controlled primarily by biological CO<sub>2</sub> fixation, indicating that biological production is most likely the main driving force in the marginal ice zone in the Southern Ocean in summer, similar to coastal oceans in other regions. However, near the zone of Antarctic divergence in Prydz Bay (about 64°S), hydrological processes rather than atmospheric processes become the controlling factors of sea surface *p*CO<sub>2</sub>. Biogeochemical tracer data suggest that upwelling of dissolved inorganic carbon from Circumpolar Deep Water (CDW) is primarily responsible for the sea surface *p*CO<sub>2</sub> distributions, which means the region outside Prydz Bay is an important source of CO<sub>2</sub> for the atmosphere. Gao et al. (2008) calculated the air–sea CO<sub>2</sub> flux in Prydz Bay to be about  $-3.23 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$  in the inner part of Prydz Bay, i.e., a sink of atmospheric CO<sub>2</sub>, and  $0.62 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$  outside the bay, i.e., a weak source of atmospheric CO<sub>2</sub>. They determined the average air–sea flux of CO<sub>2</sub> in Prydz Bay to be  $-2.50 \text{ m}^{-2}\cdot\text{a}^{-1}$ .

#### 3.2 Southern Ocean

The Southern Ocean, defined here as the oceanic region south of 50°S, is one of the most important regions in the global carbon cycle. It has been suggested that the Southern Ocean represents the largest sink region for anthropogenic CO<sub>2</sub> in the world's oceans because of the large cold surface area, high wind velocity, and high export of organic carbon to deeper layers of the ocean (Sabine and Mackenzie, 1991; Takahashi et al., 2006; McNeil et al., 2007). However, because of limited *in situ* measurements and insufficient sampling, the rate of CO<sub>2</sub> uptake from the atmosphere in this region remains uncertain and it cannot be assessed satisfactorily (Takahashi et al., 2006).

Gao et al. (2001) took advantage of China's Antarctic scientific expeditions between Zhongshan Station in East Antarctica and Great Wall Station on the Antarctic Peninsula to calculate the CO<sub>2</sub> source/sink distribution of the ice zone in the Southern Ocean and of its sea–air flux between 60°W and 80°E in the austral summer. Their results revealed a sink for atmospheric CO<sub>2</sub> during summer between 80°W and 80°E in the Southern Ocean, which was especially strong in the areas of 40°W to 30°E and 10°W to 10°E. A similar pattern of sink distribution was also observed based on observations during the return from Great Wall Station to Zhongshan Station. The absorption of atmospheric CO<sub>2</sub> by the sea in the investigated waters in

January was twice that in December. Using the latest method for the calculation of the transfer velocity of CO<sub>2</sub>, the fluxes of CO<sub>2</sub> were determined as 3.98 and 2.13 mol·m<sup>-2</sup>·a<sup>-1</sup> in January and December respectively. The average total CO<sub>2</sub> flux in the Southern Ocean during summer was 3.06 mol·m<sup>-2</sup>·a<sup>-1</sup>, suggesting this region to be an important summertime sink of CO<sub>2</sub> in the Southern Hemisphere.

Chen et al. (2011) reported an extrapolative method used to compute air–sea flux in the southern Atlantic Ocean and Indian Ocean. Empirical relationships were derived between *in situ* pCO<sub>2</sub> and Chl-*a* measurements and sea surface temperature (SST) data along cruise tracks from Zhongshan Station and Great Wall Station in December 1999, January 2000, December 2004, and January 2005 during the CHINARE-16 and CHINARE-21 campaigns. These empirical relationships were applied to datasets of remotely sensed Chl-*a* and SST to estimate both the monthly air–sea carbon flux and the uptake of atmospheric CO<sub>2</sub> in the southern Atlantic and Indian oceans. The results showed significant spatiotemporal variability of carbon flux. The monthly uptakes of atmospheric CO<sub>2</sub> in the region from 50°S to the ice edge between 60°W and 80°E were -0.00355, -0.00573, -0.00361, and -0.00525 GtC in December 1999, January 2000, December 2004, and January 2005, respectively.

In the work by Chen et al. (2011), the marine pCO<sub>2</sub> was found to be correlated negatively with Chl-*a* in the South Atlantic Ocean and the southern Indian Ocean, and it showed negative correlation with respect to SST in upwelling zones. The pCO<sub>2</sub>–Chl-*a* relationships were used to account for the biological effects, while the use of SST accounted for the mixing, upwelling, and thermodynamic effects. The biological contribution might be more evident in an SST-dominant region because biological activity tends to be higher in warmer water, while a physical contribution might be included in a Chl-*a*-dominant region because mixing affects biology (Rangama et al., 2005).

Based on underway measurements of pCO<sub>2sw</sub> (µatm) in 2009 during the CHINARE-26, Xu et al. (2016) found that pCO<sub>2sw</sub> was significantly lower in the Atlantic and Indian ocean sectors of the Southern Ocean than in the Pacific Ocean sector (Figure 1a). Moreover, pCO<sub>2sw</sub> showed different relationships with Chl-*a* and SST depending on the regional Chl-*a* value. Thus, they derived empirically a Chl-*a* threshold of 0.5 mg·m<sup>-3</sup>. During the study period, it was found that pCO<sub>2sw</sub> correlated negatively with Chl-*a* in regions where the Chl-*a* value was greater than the threshold. When Chl-*a* values were smaller than the threshold, it was found that pCO<sub>2</sub> correlated with Chl-*a* and SST with *r*<sup>2</sup> values of 0.63 and 0.76 in November and December 2009, respectively. Including the effects of sea ice, Xu et al. (2016) estimated a Southern Ocean CO<sub>2</sub> source to the atmosphere in November 2009 of about 1.65 Tg·C, with uncertainty of ±0.73 Tg·C based on an uncertainty propagation formula. However, in December

2009, they estimated a CO<sub>2</sub> sink of -2.34 Tg·C, with uncertainty of ±1.03 Tg·C. In austral summer, the South Atlantic Ocean and the South Pacific Ocean remain strong carbon sinks. When compared with the monthly climatological results of Takahashi et al. (2012), the results of Xu et al. (2016) revealed a similar distribution of sea–air carbon flux.

#### 4 Distributions of N<sub>2</sub>O and its air–sea fluxes in Prydz Bay

The ocean, particularly the Southern Ocean, is considered a significant source of atmospheric N<sub>2</sub>O, an ozone-depleting greenhouse gas. The radiative forcing of N<sub>2</sub>O is 200–300 times greater than CO<sub>2</sub> on a molecular basis. Much progress has been made in studies on marine N<sub>2</sub>O during the previous 50 years (Bange, 2008). The results have shown that oceanic N<sub>2</sub>O contributes about one third of the global budget. However, the Southern Ocean accounts for 20% of the area of the world's oceans, and the fact that it has not been studied well, because of its inherently rough conditions, is expected to have considerable ramifications on climate modeling. The scarcity of data obtained from the Southern Ocean results in uncertainty in modelling studies, which is a problem that must be addressed in the future.

A limited number of studies have been performed in the Southern Ocean (Priscu et al., 1990; Rees et al., 1997; Abollino et al., 2001; Farias et al., 2007; Zhan and Chen, 2009; Boontanon et al., 2010; Zhan et al., 2015), two of which have been conducted by Chinese scientists in the past decade. Zhan et al. (2009) analyzed the surface seawater N<sub>2</sub>O concentrations during the CHINARE-22 (November 2005 to March 2006). Their results showed that the concentration of N<sub>2</sub>O in surface seawater increased from 8.9 ± 0.2 to 17.9 ± 0.3 nM along the cruise tracks southward from 30°S to 67°S (Figure 2a), and that the surface water N<sub>2</sub>O concentration correlated well with SST. The saturation state of surface water along the cruise tracks varied from undersaturated (south) to oversaturated (north) with the turning point located between 50° and 55°S, coincident with the location of the Subantarctic Front (SAF). Oversaturation of N<sub>2</sub>O found to the north of the SAF is due to seasonal SST variation, while undersaturation south of the SAF might be due to a combination of SST variation and the intrusion of N<sub>2</sub>O-depleted ice meltwater during summer. Sea to air fluxes measured on cruise tracks to the north of the SAF ranged between 5 and 10 µmol·m<sup>-2</sup>·d<sup>-1</sup>, while fluxes south of the SAF were close to zero. The N<sub>2</sub>O in the surface water of Prydz Bay was found in near equilibrium with the atmosphere; the corresponding air–sea flux was about -0.3 ± 0.8 µmol·m<sup>-2</sup>·d<sup>-1</sup>, i.e., not significantly different from zero.

Recent work conducted by Zhan et al. (2015) during the CHINARE-27 in January 2011 showed that the distribution of N<sub>2</sub>O in Prydz Bay differed between the

northern and southern sides of the Antarctic Slope Front, corresponding to the different hydrographic characteristics on each side (Figure 2b). They specifically highlighted that although the air to sea  $N_2O$  flux to the north of the shelf break is approximately  $-1.20 \pm 0.44 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , the source/sink characteristics need to be constrained further because the CDW might occasionally outcrop over the surface layer and present as a source. The water masses over the continental shelf to the south of the shelf break might be a temporary, or even permanent,  $N_2O$  sink when sea ice is absent. The air to sea flux to the south of the shelf break is approximately  $-3.65 \pm 0.95 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , and the water column is undersaturated with  $N_2O$ , which might result from deep convection of  $N_2O$ -undersaturated surface water during winter. Evidence also suggests that the formation of Antarctic Bottom Water (AABW) might provide a pathway for  $N_2O$  removal from the upper layers at high latitudes.

## 5 Isotopic oceanography

The Chinese program of observation and research of isotopic oceanography in the Southern Ocean began with the CHINARE-06 in 1989, during which the oxygen isotopic compositions of the surface waters in Prydz Bay and its adjacent seas were analyzed. Later, during the CHINARE-13 in 1996, isotopic observation and research in the Southern Ocean became more systematic. Under the leadership and organization of the Chinese Arctic and Antarctic Administration, SOA and the Polar Research Institute of China, the analyses of marine isotopic compositions as well as the tracing of oceanographic processes in Prydz Bay and its adjacent seas were conducted during the CHINARE-13, CHINARE-14, CHINARE-15, CHINARE-16, CHINARE-18, CHINARE-20, CHINARE-22, and CHINARE-24, CHINARE-25, CHINARE-26, CHINARE-27, CHINARE-28, CHINARE-29, CHINARE-30. The targeted nuclides included natural radionuclides (i.e.,  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{234}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{210}\text{Po}$ , and  $^{210}\text{Pb}$ ), artificial radionuclides (i.e.,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{90}\text{Sr}$ , and  $^{137}\text{Cs}$ ), and stable isotopes (i.e.,  $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$ ). Based on past studies along the cruise tracks and in Prydz Bay and its adjacent seas, a series of important findings concerning isotopic distributions and their oceanographic implications have been achieved. For example, a “double-peak” feature in the latitudinal  $\delta^2\text{H}$  distribution within the surface waters of the Southern Ocean was revealed. Furthermore, significant variations of surface  $^{226}\text{Ra}$  activity between the areas to the north and south of the Antarctic Convergence Zone were detected (Yin et al., 2004; Chen et al., 2011). Other findings included establishing the conservative behavior of uranium in the surface waters of Prydz Bay (Yin et al., 2004), quantifying the negative relationship between bacterial production and dissolved organic carbon (Qu et al., 2004; Peng et al., 2005), and revealing the

latitudinal variability of nitrogen fixation rates and particle  $\delta^{15}\text{N}$  signals (Zhang et al., 2011). Several other innovative achievements have also been accomplished. These include the use of isotopic tracers for assessment of water mass structures in Prydz Bay and its adjacent seas, estimation of water mass movement and transport under the Amery Ice Shelf based on radium nuclides, assessment of the implications of AABW outside Prydz Bay, and determination of the spatial variation of the biological pump between the inner areas of Prydz Bay and areas outside, all of which have promoted deeper understanding of the hydrography and biogeochemistry of the Southern Ocean.

### 5.1 Isotopic tracers for water mass structures in Prydz Bay and its adjacent seas

Since the CHINARE-06, several cruises have been conducted to explore the seawater  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of Prydz Bay and its adjacent areas (Yin et al., 2004; Peng et al., 2005; Chen et al., 2011), and to characterize the variance of isotopic compositions and the geochemical patterns of the major water masses in and around Prydz Bay. Based on the typical  $\delta^2\text{H}$  features of the CDW, a three end-member mass balance model comprising the CDW, ice sheet (or snow) meltwater, and sea ice meltwater was applied to quantify the fractions of the latter two components in and around Prydz Bay. It was established that during austral summer 1996, the fraction of ice sheet (or snow) meltwater was 0.00%–3.82% and that of sea ice meltwater within –3.20% to 4.80% (Cai et al., 2003).

### 5.2 Isotopic fingerprints of AABW outside Prydz Bay

The formation of AABW has always been one of the most important issues among the Southern Ocean research. Based on plots of salinity vs.  $\delta^{18}\text{O}$  (S- $\delta^{18}\text{O}$ ) and salinity vs.  $\delta^2\text{H}$  (S- $\delta^2\text{H}$ ), the AABW signal was discovered above the Antarctic continental slope as well as in the deep basin outside of Prydz Bay during the CHINARE-15. It is possible that saline, dense, and cold Antarctic Shelf Water (SW) sinking down the shelf slope and mixing with CDW causes the formation of AABW. No direct evidence of SW sinking was observed during the cruise; therefore, it was speculated that AABW formation probably occurred in austral winter. In contrast, signs of the formation of AABW by CDW and SW mixing were absent according to the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  distributions collected during the CHINARE-13 and CHINARE-14. The dissimilar results obtained during the CHINARE-13, CHINARE-14, and CHINARE-15 cruises were probably due to differences in sampling sites and sampling depths, or to interannual variance in AABW formation.

During the CHINARE-26 (December 2009 to February 2010), the AABW signal was found to occur near the bottom layers of the lower slope of the P2, P3, and P4

sections (Figure 1c), corresponding to depths below 2300 m. The observed water mass temperature was lower than 0°C, salinity was 34.66–34.67, and the average  $\delta^{18}\text{O}$  was  $-0.16\%$ . Based on the relationship between salinity and  $\delta^{18}\text{O}$ , this suggested that AABW might form entirely from mixing of the High Salinity Shelf Water (HSSW) in Prydz Bay with the CDW outside the bay.

### 5.3 Significant differences of primary production in and around Prydz Bay

The  $^{14}\text{C}$ -uptake incubation has been used in several Antarctic expeditions to measure the primary productivity of Prydz Bay and of its adjacent seas. This was found to vary considerably over wide time scales ranging from  $<1$  d to  $>10$  a (Qiu et al., 2004). However, the spatial primary productivity could be characterized by markedly higher values at both the ice edge and the shelf region inside Prydz Bay in comparison with the slope area and the deep basin outside the bay, especially near 67°S corresponding to a front of sharp gradient. This suggests that water column stability might be one of the primarily factors regulating the variability of primary productivity between Prydz Bay and the areas outside areas, because shallower mixing depths favor phytoplankton photosynthesis in upper layers where light is more available; thus, enhancing the fixation of biological carbon (Zhang et al., 2014).

During the CHINARE-18, the study of  $^{210}\text{Po}/^{210}\text{Pb}$  disequilibria outside Prydz Bay suggested that  $^{210}\text{Po}$  was deficient relative to its parent  $^{210}\text{Pb}$  in surface layers. In the subsurface or middle layers,  $^{210}\text{Po}$  exhibited excess, and the specific particulate  $^{210}\text{Po}$  activity correlated positively with particulate organic carbon (POC) (Yang et al., 2009). This confirmed that the deficit and excess of  $^{210}\text{Po}$  relative to its parent  $^{210}\text{Pb}$  could be applied to indicate the export and remineralization of particulate organic matter. Based on the  $^{210}\text{Po}/^{210}\text{Pb}$  disequilibria outside Prydz Bay, the POC export flux at 100 m was calculated as  $2.3 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  (Frölicher et al., 2015), consistent with estimates from the pelagic Southern Ocean of the Indian Ocean sector (i.e.,  $0.10$ – $2.53 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), quantified by  $^{234}\text{Th}/^{238}\text{U}$  disequilibria (Coppola et al., 2005). Thus, this means the POC export flux outside Prydz Bay is relatively low. During the CHINARE-22 (November 2005 to March 2006), POC export flux at 25/50 m in Prydz Bay and its adjacent seas was estimated to be within  $29.5$ – $262.4 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , according to the  $^{234}\text{Th}/^{238}\text{U}$  disequilibria of five stations (located along a section at 73°E), with greater flux in the bay than outside (He et al., 2007).

### 5.4 Variation of biological pump in and outside Prydz Bay induced by physical–biological coupling

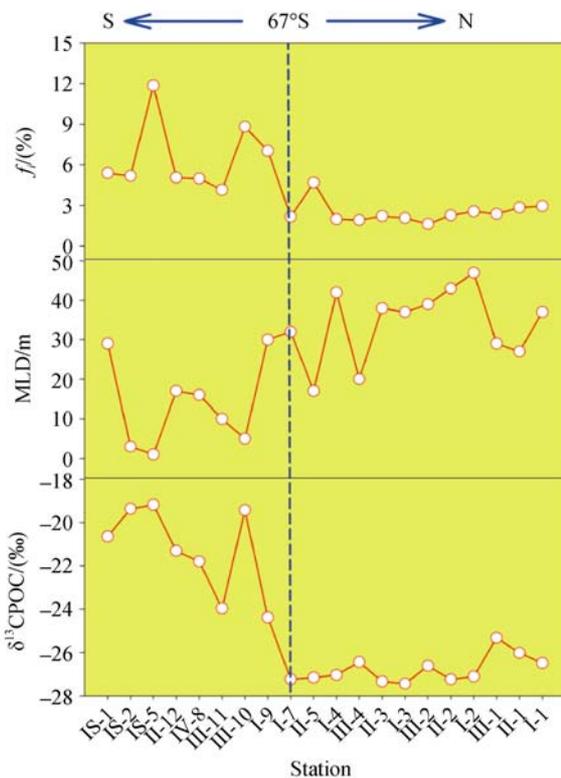
The variation of the biological pump between inner and outer areas of Prydz Bay can be verified by the distribution of stable carbon isotopes in the POC, from

which the variability of the biological pump induced by physical–biological coupling can be revealed. In the CHINARE-22 during summer 2006, obvious differences in the isotopic features between the inner and outer areas of Prydz Bay were observed. It was found that surface  $^{226}\text{Ra}$  activity outside Prydz Bay was higher than inside the bay, which was correlated with interactions between high  $^{226}\text{Ra}$  concentration CDW and low  $^{226}\text{Ra}$  concentration sea ice meltwater. In addition, values of  $\delta^{13}\text{C}_{\text{POC}}$  measured outside the bay were lower than inside the bay, especially in the area north of 67° (i.e., lower values and small range:  $-25.3\%$  to  $-27.5\%$ ). For comparison, the values of  $\delta^{13}\text{C}_{\text{POC}}$  in the bay were all larger than  $-22.0\%$ , with the highest measurement recorded close to the Amery Ice Shelf. The  $\delta^{13}\text{C}_{\text{POC}}$  was found correlated positively with both the fraction of sea ice meltwater and the POC concentration but found correlated negatively with macronutrients. This suggests that the spatial patterns of  $\delta^{13}\text{C}_{\text{POC}}$  both inside and outside Prydz Bay are regulated by physical–biological coupling, i.e., the increase of sea ice meltwater strengthens water column stability, leading to an environment more suitable for algal growth; thus, enhancing primary production. Elevated levels of productivity deplete the macronutrients and reduce the dissolved  $\text{CO}_2$  in seawater. This weakens the isotopic fractionation of inorganic carbon uptake during algal photosynthesis, and increases the  $\delta^{13}\text{C}_{\text{POC}}$  in produced POC (Figure 3) (Zhang et al., 2014). Physical–biological coupling is proposed as an essential force that drives the observed chemical and biological variations both inside and outside Prydz Bay. The increase of sea ice meltwater leads to greater stability of the water column in Prydz Bay compared with outside the bay. This promotes algal production inside the bay, which causes the observed differences in both the isotopic features and the biological pump between the areas inside and outside the bay.

## 6 Antarctic marine aerosol research

Aerosol research started with the development of the Chinese National Expedition program. In the CHINARE-01 expedition, Chen et al. (1993) collected 31 aerosol samples near the Antarctic Peninsula and over the Pacific Ocean using an SH-I aerosol sampler. In CHINARE-03, they collected 50 aerosol samples during the cruise near the Antarctic Peninsula and over the Pacific, Atlantic, and Indian oceans using modified SH-I samplers.

In addition, further aerosol samples were collected during a cruise to Antarctica by a polar research vessel. The contents of Na, Mg, K, Cl, Ca, Br, F, and metal were analyzed, and the sources and fluxes of the chemical species were investigated (Chen et al., 1993, 1994). In 1998, a long-term marine aerosol monitoring station was established at Zhongshan Station (Wang et al., 2009).



**Figure 3** Differences of ice meltwater fraction ( $f_i$ ), mixing layer depth (MLD), and  $\delta^{13}\text{C}_{\text{POC}}$  in and outside Prydz Bay in summer (Zhang et al., 2014).

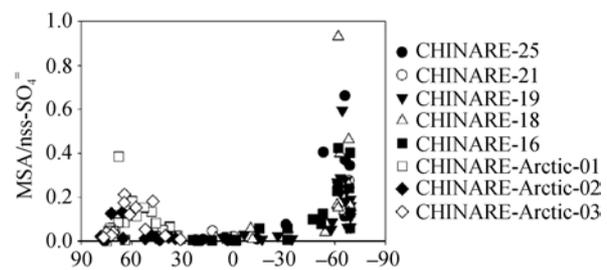
### 6.1 Marine aerosol sulfur characteristics

DMS is oxidized to non-sea-salt sulfate ( $\text{nssSO}_4^-$ ) and methane sulfonic acid (MSA) aerosols after ventilation, which comprise major sources of cloud condensation nuclei in an unpolluted marine atmosphere such as the Southern Ocean (Ayers and Gras, 1991). These aerosols have potential to interact with incoming solar radiation, which could affect their roles in cloud microphysics processes and result in a negative climate feedback mechanism (Charlson et al., 1987).

CHINARE sulfur research has focused on DMS-related aerosols (Chen et al., 2012), whereas studies of DMS measurements made in seawater and in sea ice are only at the initial stages. The lack of *in situ* measurements of DMS in seawater has led to uncertainty in the water-atmosphere flux of DMS. The development of remote-sensing technology provides the possibility of long-term, large-scale monitoring of sea surface DMS. The estimation of DMS could be calculated based on the level of chlorophyll at the sea surface.

Chen's group has been studying aerosols on the CHINARE cruises for decades and they have compared the distributions of chemical species in the aerosols to the results of the CHINARE-01 cruise. The latitudinal distributions of  $\text{MSA}/\text{nssSO}_4^-$  of CHINARE-02 were consistent with those of the first Chinese National Arctic

Research Expedition (CHINARE-Arctic-01), peaking at 50–60 and decreasing with increasing latitude. The ratios of  $\text{MSA}/\text{nssSO}_4^-$  in both hemispheres have clear trends that increase with latitude but they exhibit different patterns. The  $\text{MSA}/\text{nssSO}_4^-$  in the Northern Hemisphere increases quickly, while in the Southern Hemisphere, the ratio increases much more slowly until 50°S. At high southern latitudes, the ratio increases abruptly and it reaches a maximum at around 60°S (Figure 4). The actual maximum detected was 0.28 at 63.18°S, 40.78°E; however, the ratio did not always maintain a high level in the region of the marine Antarctic, and at 54.31°S, 178.33°W, it was found to decrease to a value as low as 0.02 (Chen et al., 2012).



**Figure 4** Spatial distributions of  $\text{MSA}/\text{nssSO}_4^-$  during five CHINARE cruises and three CHINARE-Arctic cruises from 1998 to 2008 (southern latitude is negative). CHINARE means Antarctic cruises and CHINARE-Arctic means Arctic cruises (Chen et al., 2012).

This latitudinal gradient of  $\text{MSA}/\text{nssSO}_4^-$  has been confirmed by many other studies (Bates et al., 1992; Davison et al., 1996), and De Mora et al. (1997) summarized the global distributions of the concentrations of MSA and  $\text{MSA}/\text{nssSO}_4^-$ . The ratio of  $\text{MSA}/\text{nssSO}_4^-$  found in this study generally agreed with the values quoted in other research, confirming the latitudinal increase trend of  $\text{MSA}/\text{nssSO}_4^-$  in the Southern Hemisphere, especially in coastal Antarctica.

The significantly high ratios of  $\text{MSA}/\text{nssSO}_4^-$  found near coastal Antarctica have been considered to be mainly due to the oxidation of marine biogenic DMS at low temperatures (Hynes et al., 1986; Rädlein and Heumann, 1992). The high strength of the DMS source and the temperature-dependent kinetics of MSA formation have been used to explain not only the DMS–MSA relationship but also the inverse relationship between MSA concentration and the ambient temperature, because lower temperature might lead to higher yield of MSA (Bates et al., 1992). Hence, at certain temperatures, the ratios of  $\text{MSA}/\text{nssSO}_4^-$  might possibly remain at certain values. Since the temperature patterns of the Northern and Southern hemispheres are similar, as shown in Figure 4, similar patterns of  $\text{MSA}/\text{nssSO}_4^-$  should be expected in both hemispheres if DMS were the main source of both MSA and  $\text{nssSO}_4^-$ . However, neither the MSA concentrations nor the  $\text{MSA}/\text{nssSO}_4^-$  ratios showed similarities with air

temperature in either hemisphere. In Arctic regions, the highest MSA values were not associated with the lowest temperature, and the correlation between MSA and air temperature was weak ( $r^2$  value of 0.033). High values of MSA concentrations occurred in areas with high DMS emission at the sea surface, but these values were unrelated to low air temperature when aerosol sampling was performed. During the Antarctic cruises, the  $\text{MSA}/\text{nssSO}_4^-$  ratios varied from 0.024 to 0.930 in the high southern latitudes, but strong relationships between MSA concentrations or  $\text{MSA}/\text{nssSO}_4^-$  and air temperature during aerosol sampling were not found. There might be factors other than temperature and DMS that contribute to the different distributions of the MSA and  $\text{nssSO}_4^-$  concentrations and of the  $\text{MSA}/\text{nssSO}_4^-$  ratio.

## 6.2 Marine aerosol heavy metal characteristics

Anthropogenic activity is one of the major factors that affects the concentrations of heavy metals in the aerosols observed at the research station. Research has indicated that dust could be detected in the snow surface 10–100 km from the station (Boutron and Wolff, 1989).

During the CHINARE-03 cruise from November 1986 to May 1987, Chen's group collected 58 aerosol samples. The contents of Na, Mg, K, Cl, Ca, Br, F, Al, V, Mn, I, Fe, Pb, Cu, and Cd of the samples were analyzed and factor analysis, principal component analysis, and cluster analysis were applied to the dataset to investigate the sources of the aerosols. The results suggested that Al is a typical crustal element, Na and Cl are of marine origin, and V is derived from continental pollution. The enrichment of Ca, Br, F in the remote atmosphere might be due to marine bioactivities and microsurface beneficiation, while in the coastal atmosphere, the concentrations of these elements exhibited a gradient trend indicative of continent transport. The relative concentrations of water-soluble metals in the coastal atmosphere were found to be  $\text{Cd} > \text{Mn} > \text{Cu} > \text{Fe} > \text{Pb}$ , with percentages of 39.0%, 36.0%, 23.0%, 14.0%, and 5.3%, respectively. The concentrations of water-soluble metals in the remote oceanic atmosphere were found to be  $\text{Cd} > \text{Mn} > \text{Fe} > \text{Cu} > \text{Pb}$ , with percentages of 62.0%, 44.0%, 11.0%, 3.1%, and 2.5%, respectively. Chen's group also estimated the air–sea fluxes of the metals (Chen et al. 1993, 1994).

During the CHINARE-16 cruise (November 1999 to April 2000), Huang et al. (2005) collected 22 aerosol samples and analyzed the concentrations of Cu, Pb, Zn, Cd, Fe, Al, Mn, Cr, V, K, Na, Ca, and Mg in the samples. Enrichment, factor analysis, and principal component analysis performed as part of their study all showed that the distributions of the metals exhibited geographic disparity and their sources were discussed.

Bulk high-volume aerosol samples were collected over three years at Zhongshan Station in East Antarctica. A graphical technique was applied to the data acquired by an instrumental neutron activation analysis spectrometer

(INAA). The results showed that Na, Cl, Mg, Ca, Sr, Br, I, Sr, and Rb were marine elements, while Al, Sc, Fe, and Mn were considered crustal elements. Five elements (Se, Co, Sb, Zn, and Cr) that were highly abundant in the station aerosols originated either from marine or crustal sources, and they might have come from the burning of fossil fuels for heating and equipment operation. The presence of these pollutant elements indicates that human activities have obviously affected local environments in Antarctica (Wang et al., 2010).

## 6.3 Fertilization experiment

The scientific principle of artificial iron fertilization of the ocean is to stimulate primary production of phytoplankton, with the objective of increasing the absorption of  $\text{CO}_2$  and ultimately increasing the carbon sink through the biological pump via particle organic carbon. There are two types of potential areas for its implementation: high-nutrient low-chlorophyll areas and low-nutrient low-chlorophyll areas. In the former, iron limits primary production of phytoplankton, while in the latter, iron might limit biological nitrogen fixation.

To study the characteristics of atmospheric soluble iron in the Southern Ocean and in Southeast Asia, Gao et al. (2013) collected large volumes and layered aerosols (diameter: 0.056–18  $\mu\text{m}$ ) from the sea area between 40°S, 100°E and 69°S, 76°E, and between 69°S, 76°E and 66°S, 110°E from November 2010 to April 2011. The average iron concentration in the Southern Ocean is 19  $\text{ng}\cdot\text{m}^{-3}$  (range: 10–38  $\text{ng}\cdot\text{m}^{-3}$ ), whereas in coastal East Antarctica (which here refers to the coastal section of Antarctica between 66°S and 69°S) it is 26  $\text{ng}\cdot\text{m}^{-3}$  (range: 14–56  $\text{ng}\cdot\text{m}^{-3}$ ). The average concentration of soluble iron (II) in the Southern Ocean is 0.22  $\text{ng}\cdot\text{m}^{-3}$  (range: 0.13–0.33  $\text{ng}\cdot\text{m}^{-3}$ ), whereas it is 0.53  $\text{ng}\cdot\text{m}^{-3}$  (range: 0.18–1.30  $\text{ng}\cdot\text{m}^{-3}$ ) in coastal East Antarctica. The total soluble iron found in the Southern Ocean or in coastal East Antarctica shows similar tendencies. The distribution of particle sizes of soluble iron (II) in the Southern Ocean exhibits a single-peak pattern; however, in coastal East Antarctica, it presents a double-peak pattern with maxima at 0.32–0.56  $\mu\text{m}$  and 5.6–10.0  $\mu\text{m}$ . Compared with the Southern Ocean, the higher iron concentrations and coarser particle sizes of Fe (II) in coastal East Antarctica indicate that the Antarctic continent might provide a source of Fe (II). The ratio of soluble Fe (II) is about 0.58% to 6.50%, and it decreases with the increase of total iron concentration. The atmospheric flux of Fe (II) in the Southern Ocean is estimated at approximately 0.007–0.092  $\text{mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ , and that in coastal East Antarctica is estimated at approximately 0.022–0.210  $\text{mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ . The atmospheric flux of total soluble iron in East Antarctica is estimated at approximately 0.07–0.52  $\text{mg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ . The input of soluble iron from the atmosphere contributes to the concentration of soluble iron in the surface waters of the Southern Ocean.

Gao et al. (2013) analyzed the atmospheric sources of

samples with the highest concentrations using backward air parcel trajectories. They found that the concentration in the coastal East Antarctica is higher than in the Southern Ocean, indicating the Antarctic continent might be the source. However, Gao et al. (2013) continued to study the distribution of iron in different particle sizes in the Southern Ocean.

## 7 Conclusions and prospects

Looking back on the active history of nearly 30 years of Chinese Antarctic expeditions, it is evident that great progress has been achieved in the field of Antarctic chemical oceanographic research. In particular, fruitful results have been obtained in the fields of the sea-surface distributions and air-sea fluxes of CO<sub>2</sub> and N<sub>2</sub>O, and regarding the transport, flux, and budget of organic matter using isotopes. Nevertheless, because of the harsh environment in the Southern Ocean and the limitations of the icebreaker R/V *Xuelong* in terms of its availability and capability, many aspects of Chinese research require strengthening.

In the field of CO<sub>2</sub>, China has already accumulated 30 years' CO<sub>2</sub> data from Southern Ocean and Prydz Bay. However, the monthly air-sea flux of CO<sub>2</sub> in the Southern Ocean has been estimated using *in situ* and remotely sensed data during only one or two cruises. Although the current situation and historical changes of CO<sub>2</sub> are known, it is necessary to improve the estimated rates and scales of change of the CO<sub>2</sub> distribution and air-sea flux in the Southern Ocean, and to evaluate links with environmental and climatic changes over the previous three decades. Furthermore, ocean acidification is occurring more rapidly in higher latitudes than lower latitudes because of the lower temperatures. Thus, much more work is needed in the field of ocean acidification.

Some progress has been made with regard to N<sub>2</sub>O during the past decade. Effort has been focused on filling the data gap regarding Southern Ocean N<sub>2</sub>O, and both upwelling of CDW and dilution effects of sea ice melting on N<sub>2</sub>O have been identified. However, despite being considered one of the most important sources of N<sub>2</sub>O, only very limited information is available. Therefore, further work is needed in the Southern Ocean, especially where upwelling of CDW occurs. Additional surveys and the acquisition of high-resolution data are planned to try to constrain the contribution of the Southern Ocean to the global N<sub>2</sub>O budget.

Among the isotopic oceanographic studies conducted in the Southern Ocean, the highly sensitive isotopic technique adopted during the CHINAREs has made a positive contribution to the understanding of the oceanographic dynamics and mechanisms of the Southern Ocean. Several significant outcomes have been achieved that have promoted deeper understanding of the hydrography and biogeochemistry of the Southern Ocean.

In particular, notable results have been achieved using isotopic tracers for assessing both the nature of the water mass structures in Prydz Bay and its adjacent seas and the implications of AABW outside Prydz Bay, as well as investigating the spatial variation of the biological pump between the inner area of Prydz Bay and areas outside. However, it remains necessary to improve the observations and to strengthen research of the key areas, time series, and isotope assemblages to consolidate the constraints both of the environmental regulation of the Southern Ocean and of its response and feedback in relation to global climate change.

The sulfur cycle is an important biogeochemical cycle of the earth system, which includes sulfur-related aerosols and DMS measurement in seawater. Currently, the spatial and temporal resolutions of data constitute the primary limiting factor restraining further development of the understanding of the sulfur cycle. Hence, the delivery of appropriate *in situ* technology is an urgent requirement for determining the spatial and temporal distributions of aerosols and seawater sulfur and for assessing their impacts in relation to global climate change. Following years of effort by Chen's group, suitable techniques are in development. Already *in situ* measurement of DMS in seawater has been conducted during the CHINARE cruises and large amounts of data have been obtained. A system for the *in situ* measurement of aerosol ions and anions was installed on the R/V *Xuelong* for the CHINARE-33.

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