

Summer and winter distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in surface waters of the South Indian Ocean [20°S–60°S]

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ABSTRACT

This paper describes for the first time the summer and winter distributions of sea surface $\delta^{13}\text{C}_{\text{DIC}}$ in the Southern Indian Ocean (20°S–60°S). For this we used $\delta^{13}\text{C}_{\text{DIC}}$ measurements from 10 cruises conducted between 1998 and 2005. For summer and winter, the highest $\delta^{13}\text{C}_{\text{DIC}}$ values ($>2\text{‰}$) are observed in sub-Antarctic waters (40°S–50°S) and attributed mainly to biological activity, enhanced in the vicinity of Crozet and Kerguelen Archipelagoes. The lowest $\delta^{13}\text{C}_{\text{DIC}}$ values are found in subtropical waters (25°S–35°S), with a minimum ($<1\text{‰}$) in the Agulhas Current region and in the Mozambique channel. On the seasonal scale, $\delta^{13}\text{C}_{\text{DIC}}$ is higher during summer than during winter in all regions. The largest seasonal amplitude of variation ($\sim 0.3\text{‰}$), observed in the region 35°S–40°S, is attributed to biological activity during summer and to deep vertical mixing during winter. In subtropical oligotrophic waters, the mean seasonal amplitude of variation ($\sim 0.15\text{‰}$) is mainly explained by air–sea CO_2 fluxes. On the interannual scale, we also identified a large negative anomaly of $\delta^{13}\text{C}_{\text{DIC}}$ in the subtropical waters during austral summer 2002, associated to an anomalous ocean CO_2 sink due to cold conditions during this period.

1. Introduction

Carbon dioxide (CO_2) emissions (from fossil fuel burning and land use change) increased strongly in recent years, from 5.5 PgC yr^{-1} ($\text{Pg} = 10^{15} \text{ g}$) in 1970 to 8.4 PgC yr^{-1} in 2000 (Raupach et al., 2007) and 9.9 PgC yr^{-1} in 2006 (Canadell et al., 2007). As a consequence, the accumulation of anthropogenic CO_2 in the atmosphere reached the benchmark of 100 ppm in 2007 (Le Quéré et al., 2009), which raises the issue of global warming and the associated climate change, the well-known consequences of increasing atmospheric CO_2 (IPCC, 2007). An evidence for this human-induced perturbation, aside from atmospheric CO_2 measurements, is the modification of the isotopic ratio of CO_2 known as the ^{13}C Suess effect. Indeed, since plants preferentially use the lightest carbon isotope (^{12}C) during photosynthesis, the burning of fossil fuel releases mainly $^{12}\text{CO}_2$ in the atmosphere (Gruber et al., 1999), resulting in a decrease in the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$). The ^{13}C Suess effect was evaluated to -0.02‰ yr^{-1} since 1988 based on atmospheric measurements (Quay et al., 1992) but modelling studies have recently shown that the magnitude of this phenomenon depends on the time frame over which it is evaluated (Tagliabue

and Bopp, 2008). As the ocean takes up between 15 and 20% of current CO_2 emissions (Takahashi et al., 2002, 2009), the ^{13}C Suess effect is nevertheless transmitted to surface waters; several studies thus showed a decrease in the $^{13}\text{C}/^{12}\text{C}$ ratio of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$, e.g. Kroopnick, 1985; Broecker and Maier-Reimer, 1992; Gruber et al., 1999; Sonnerup et al., 2000; McNeil et al., 2001; Quay et al., 2003; Tagliabue and Bopp, 2008). This signal, the oceanic ^{13}C Suess effect, reflects the accumulation of anthropogenic CO_2 in the ocean, and therefore provides an additional constraint for estimating the global carbon budget. Consequently observing and understanding the seasonal to decadal variability of both atmospheric CO_2 and ^{13}C budget could help in separating the carbon sources and sinks at planetary scale between land and ocean systems (e.g. Ciais et al., 1995). On the ocean side, despite regular observations conducted since 1980s at few time-series stations and during WOCE/JGOFS era (1990s), the seasonal variability of surface $\delta^{13}\text{C}_{\text{DIC}}$ is not yet very well described at global ocean scale. In the high northern latitudes of the North Atlantic ocean the winter/summer difference of $\delta^{13}\text{C}_{\text{DIC}}$ may be as large as $\sim 1\text{‰}$ (Gruber et al., 1999) that potentially masked the ^{13}C Suess effect observed in the surface water (McNeil et al., 2001). It has been also suggested from ocean carbon models, that upwelling of deep waters brings an older $\delta^{13}\text{C}_{\text{DIC}}$ signal from the atmosphere in the surface layers and thus dilutes the ocean ^{13}C Suess effect (Tagliabue and Bopp, 2008). In these models, processes such as biological activity, thermodynamics and ocean circulation that

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control the ocean $\delta^{13}\text{C}_{\text{DIC}}$ distribution (and ocean CO_2) in the surface and deep waters, need to be compared against seasonal $\delta^{13}\text{C}_{\text{DIC}}$ fields in order to best represent the $\delta^{13}\text{C}_{\text{DIC}}$ distribution that could be used for both geological (testing the proxies) and predictive simulations including the coupling between climate and carbon changes. Understanding better the temporal evaluation of surface $\delta^{13}\text{C}_{\text{DIC}}$ distribution and the driving processes would also reduced uncertainties when using $\delta^{13}\text{C}_{\text{DIC}}$ observations to evaluate the anthropogenic CO_2 uptake in the ocean (Quay et al., 1992, 2003; Tans et al., 1993; Gruber et al., 1999; Sonnerup et al., 2000, 2007; McNeil et al., 2001; McNeil and Tilbrook, 2009).

Since about two decades, $\delta^{13}\text{C}_{\text{DIC}}$ was regularly sampled at the time-series stations Hawaii Ocean Time Series (HOTS, 23°N – 158°W) and Bermuda Atlantic Time Series (BATS, $31^\circ40'\text{N}$ – $64^\circ10'\text{W}$). These time-series provided a long-term monitoring of $\delta^{13}\text{C}_{\text{DIC}}$ that allowed to investigate the seasonal, interannual and decadal variability of $\delta^{13}\text{C}_{\text{DIC}}$ and to identify the driving processes. At station BATS, authors estimated a surface $\delta^{13}\text{C}_{\text{DIC}}$ decrease of $-0.025\text{‰ yr}^{-1} \pm 0.002\text{‰}$ (Gruber et al., 1998, 1999; Quay et al., 2003) between 1984 and 1993 and validated oceanic models which evaluate the anthropogenic carbon uptake in the ocean (e.g. Box Diffusion Model of Bascatow et al., 1996). $\delta^{13}\text{C}_{\text{DIC}}$ measurements were also collected in other oceanic regions during GEOSECS expedition (Geochemical Ocean SEction Study) at the end of 1970s, Transient Tracers in the Ocean cruises (TTO) in the 1980s, international World Ocean Circulation Experiment program (WOCE) in the 1990s, as well as during several national initiatives. The synthesis of these observations have shown a large spatial variability in both $\delta^{13}\text{C}_{\text{DIC}}$ distribution and associated oceanic ^{13}C Suess effect (e.g. Gruber et al., 1999; Sonnerup et al., 2000; Quay et al., 2003). Most of these studies focused on two major processes to explain the observed $\delta^{13}\text{C}_{\text{DIC}}$ variability in surface waters, the air–sea gas exchange and the biological activity (organic matter production/respiration and calcium carbonate formation/dissolution); however, recent modelling work also highlighted the importance of ocean circulation and mixing, especially in the high latitudes where $\delta^{13}\text{C}_{\text{DIC}}$ data are sparse (Tagliabue and Bopp, 2008).

In the Southern Ocean, the seasonality of $\delta^{13}\text{C}_{\text{DIC}}$ as well as the oceanic ^{13}C Suess effect remains poorly quantified due to the lack of good spatial and temporal coverage of $\delta^{13}\text{C}_{\text{DIC}}$ measurements (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995; Gruber et al., 1999; McNeil et al., 2001; Tagliabue and Bopp, 2008). Studies of the distribution of $\delta^{13}\text{C}_{\text{DIC}}$ and the processes controlling its evolution on seasonal to decadal scales are needed, in this region in particular, to provide insights into the ocean carbon cycle and its evolution in recent years (Le Quéré et al., 2009; Lenton et al., 2009; Metzl, 2009), and to help reducing the uncertainty in anthropogenic carbon estimates in the Southern Ocean (Lo Monaco et al., 2005; Vazquez-Rodriguez et al., 2009).

Since 1998, surface and water column $\delta^{13}\text{C}_{\text{DIC}}$ observations were collected one or twice a year in the Southwest Indian Ocean in the frame of the OISO program (Océan Indien Service d'Observation). Our study aims at providing and describing the distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in an undocumented area, for both austral summer and winter. Such analysis complements the times series of $\delta^{13}\text{C}_{\text{DIC}}$ mainly conducted in the subtropics since two decades. Here, we evaluate for the first time the mean distribution and the summer/winter variations of $\delta^{13}\text{C}_{\text{DIC}}$ in this region (20°S – 60°S) by analysing surface measurements obtained over the period 1998–2005. Following the method of $\delta^{13}\text{C}^*$ developed by Gruber et al. (1999), we also try to identify processes controlling the $\delta^{13}\text{C}_{\text{DIC}}$ distribution in the surface ocean of this region. It is our hope that these results will help to evaluate the oceanic uptake of anthropogenic carbon in this region and to constrain and validate atmospheric inversions and ocean carbon models.

2. Data collection

This work is based on observations collected over the period 1998–2005 during ten OISO cruises, including three winter cruises (Table 1), conducted on board the *R.S.S. Marion Dufresne* in the South Indian Ocean (20°S – 60°S , Fig. 1). The OISO program aims at documenting and understanding the changes observed in oceanic CO_2 from the seasonal to the decadal scale (Metzl et al., 2006; Metzl, 2009). Continuous measurements of surface CO_2 fugacity ($f\text{CO}_2$), sea surface temperature (SST) and salinity (SSS), fluorescence, dissolved inorganic carbon (DIC) and total alkalinity (TA) were performed along repeated routes between La Réunion and the sub-Antarctic islands of Crozet, Kerguelen and Amsterdam (Table 1 and Fig. 1). In addition, surface samples were collected every four or eight hours for measurements of $\delta^{13}\text{C}_{\text{DIC}}$, chlorophyll-a concentration (chl-a) and nutrients (nitrate+nitrite and silicate). In this work, we increased the surface data set by including the surface bottle data ($<20\text{ m}$) collected during CTD stations (conductivity–temperature–depth, Seabird 911 and rosette equipped with 24 Niskin bottles). Except for $\delta^{13}\text{C}_{\text{DIC}}$, instrumental techniques for seawater properties have been previously described (Jabaud-Jan et al., 2004; Metzl et al., 2006; Metzl, 2009).

Water samples collected in 125 ml glass bottles for $\delta^{13}\text{C}$ measurements were poisoned with HgCl_2 (1 ml of saturated solution) for storage, and analysed back in the laboratory. Because $\delta^{13}\text{C}$ is measured on dried CO_2 gas, water samples are first treated with phosphoric acid (H_3PO_4 85%) to change HCO_3^- and CO_3^{2-} into dissolved CO_2 (Kroopnick, 1974) before extracting the total CO_2 from sea water samples. The isotopic composition of CO_2 was determined using a dual inlet-isotopic ratio mass spectrometer (SIRA9-VG) by comparing the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample (R) to the $^{13}\text{C}/^{12}\text{C}$ ratio of a reference material (R^*), the Vienna-Pee Dee Belemnite (V-PDB). The isotopic ratio is expressed in the

Table 1. Cruises and Sampling regime

Cruise	Date	Transect	Sample
Winter			
OISO 2	18 Aug 1998 to 10 Sept 1998	R-A-K-C-R	Surface and water column (3 to 10 + 13 + 15 to 17)
OISO 5	19 July 2000 to 16 Aug 2000	R-A-K (+60S)-C-R	CTD (1 to 4 + 7 + 9 to 11 + 15 to 17)
OISO 9	22 Aug 2002 to 18 Sept 2002	R-A-K-C-R	Surface and water column
Summer			
OISO 1	21 Jan 1998 to 19 Feb 1998	R-A-K (+ South)-C-R	CTD (1 to 10 + 12 to 16)
OISO 3	4 Dec 1998 to 30 Dec 1998	R-A-K (+ South)-C-R	Surf CTD (1 + 3 to 16)
OISO 4	15 Jan 2000 to 9 Feb 2000	R-A-K (+ South)-C-R	CTD (1 to 17 + 60 to 61)
OISO 6	3 Jan 2001 to 26 Jan 2001	R-A-K (+ South)-C (+West)	Surface and water column CTD (6 to 7 + 9 to 17)
OISO 8	4 Jan 2002 to 1 Feb 2002	R-A-K (+ South)-C (+West)	Surface
OISO 11	3 Jan 2004 to 9 Feb 2004	R-A-K (+ South)-C-Mozambique channel	Surface and water column (6 to 7 + 10 to 11 + 23 + 25 + 60)
OISO 12	11 Jan 2005 to 22 Feb 2005	R-A-K (+ East)-C-R	Surf CTD (6 to 10)

Note: R: La Réunion, A: Amsterdam, K: Kerguelen and C: Crozet.

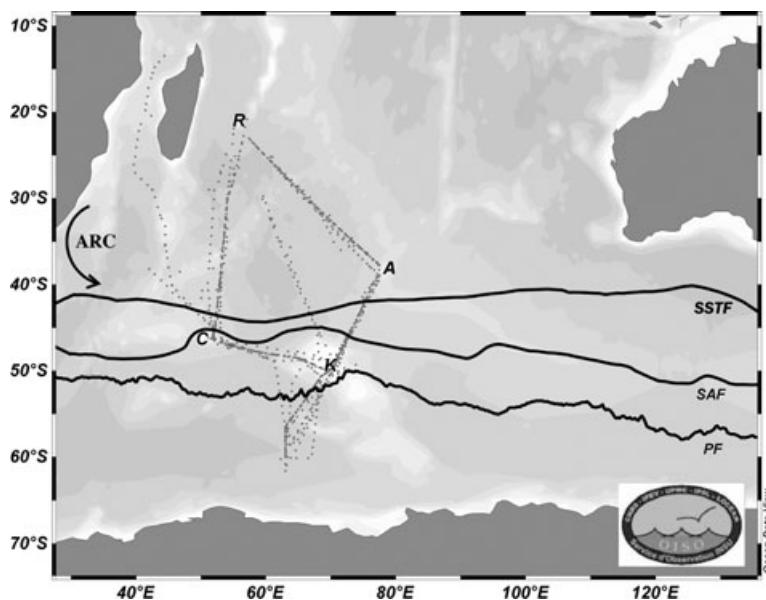


Fig. 1. Track of OISO cruises (Océan Indien Service d'Observation) conducted in summer and winter over the period 1998–2005 between La Réunion (R), Amsterdam (A), Kerguelen (K) and Crozet (C) and position of major fronts. SSTF: southern subtropical front; SAF: sub-Antarctic front; PF: polar front; ARC: agulhas return current. (Moore et al., 1999; Orsi et al., 1995; Schlitzer, 2002).

δ -unit defined by Craig (1957), as follows:

$$\delta^{13}\text{C}_{\text{DIC}}(\text{‰ vs V-PDB}) = [(R/R^*) - 1] \times 1000. \quad (1)$$

The standard deviation of $\delta^{13}\text{C}_{\text{DIC}}$ measurements is around 0.01‰.

3. Hydrological and biogeochemical context

3.1. Major hydrological fronts and water masses

This study covers the western part (40°E–80°E) of the Southern Indian Ocean from 20°S to 60°S, where three major hydrological fronts are observed (Fig. 1): the Subtropical Front (STF, or subtropical convergence) that separates the warm Subtrop-

ical Surface Water (STSW) from sub-Antarctic Surface Water (SASW) to the South, the sub-Antarctic Front (SAF), located around 45°S, and the Polar Front (PF, or Antarctic convergence), located around 50°S (e.g. Belkin and Gordon, 1996; Moore et al., 1999). In the Southwest Indian Ocean, the frontal zone is also characterized by the confluence of the agulhas front (AF), the southern arm of the STF (SSTF) and the SAF. This singular hydrological structure, known as the Crozet Front, results from the specific topography of this region (Fig. 1). The Crozet Front is characterized by a strong thermal and salinity gradient (from 20 to 9 °C and from 35.5 to 33.7), one of the most pronounced front in the Southern Ocean (Belkin and Gordon, 1996). This structure expands from the North of Crozet Islands (46°S, 51°E) to 55°E.

Table 2. Oceanic regions and their hydrological characteristics: SSS (sea surface salinity) and SST (sea surface temperature in $^{\circ}\text{C}$)

Region	Hydrological characteristics	
	Summer	Winter
Subtropical zone (STZ) North of 35°S	$35.00 < \text{SSS} < 35.50$ $\text{SST} > 20$	$\text{SST} > 14$
Transition zone (TZ) 35°S – 40°S	$35.00 < \text{SSS} < 35.50$ $15 < \text{SST} < 20$	$13 < \text{SST} < 16$
Frontal zone		
Sub-Antarctic zone (SAFZ) 40°S – 45°S	$33.85 < \text{SSS} < 35.00$ $6 \text{ (East)} / 8 \text{ (West)} < \text{SST} < 15$	$5 < \text{SST} < 15$
Polar frontal zone (PFZ) 45°S – 50°S	$\text{SSS} < 33.85$ $4 < \text{SST} < 9$	$2 < \text{SST} < 5$
Antarctic zone (AAZ) South of 50°S	$\text{SSS} > 33.8$ $\text{SST} < 4$	

In this study, we divided the region into five zones, based on the temperature and salinity characteristics of surface waters (Table 2): (i) the subtropical zone (STZ) North of 35°S , (ii) the transition zone (TZ) between warm, oligotrophic subtropical waters and colder, well ventilated, High-Nutrient-High-Chlorophyll sub-Antarctic waters (35°S – 40°S), (iii) the frontal zone (FZ) between 40°S and 50°S , and (iv) the Antarctic zone (AAZ) South of the PF (50°S). The biogeochemical characteristics for each zone are summarized in the following section, largely based on previous studies that described seasonal to decadal variations of air–sea CO_2 fluxes (Metzl et al., 1998, 2006; Metzl, 2009).

3.2. Biogeochemical regions

Sea surface $\delta^{13}\text{C}_{\text{DIC}}$ distribution is controlled by air–sea CO_2 exchange, biological productivity, vertical mixing and sea surface temperature. The relative dominance of these processes varies depending the region and seasons. Here we describe briefly the main biogeochemical seasonal characteristics for the zones identified in the previous section along with the summer/winter change of the mixed-layer depth (MLD). These are synthesized in Fig. 2 for both chl-*a* and fugacity of CO_2 ($f\text{CO}_2$), in Fig. 3 for both Nitrate (NO_3^-) and normalized DIC (nDIC) and in the Table 3 for the MLD observed in Southwest Indian surface waters.

3.2.1. Subtropical zone (North of 35°S). The subtropical zone is characterized by warm, oligotrophic waters, with a strong seasonality of the surface $f\text{CO}_2$ (Fig. 2). In summer, $f\text{CO}_2$ is generally near equilibrium with the atmosphere, whereas in winter this region is a sink for atmospheric CO_2 . The seasonal cycle of $f\text{CO}_2$, with an amplitude of 50 – $70 \mu\text{atm}$, is mainly attributed to the warming/cooling of surface waters (Metzl et al., 1998,

2006). North of the Subtropical Front, in the latitudinal band 30°S – 35°S , the mixed layer can deepens down to $\sim 150 \text{ m}$ during winter (Metzl et al. 1998; Table 3), which brings nutrients to the surface layer (from 1 to $3 \mu\text{mol kg}^{-1}$ for NO_3^- ; Fig. 3b) and enhanced biological activity, as revealed by satellite maps of chlorophyll-*a* (chl-*a* $> 0.2 \text{ mg m}^{-3}$, Figs 2 and 3a). The deepening of the mixed layer in winter also brings DIC to the surface layer (Fig. 3c), which should increase $f\text{CO}_2$ and reduce $\delta^{13}\text{C}_{\text{DIC}}$, whereas biological activity would have the opposite effect.

3.2.2. Transition zone (35°S – 40°S). The transition zone is characterized by meridional gradients in all biogeochemical properties which are opposite in summer and winter (Figs 2 and 3). During summer, the sharp decrease of $f\text{CO}_2$ southwards is related to cooling and productivity, whereas during winter, $f\text{CO}_2$ increases southwards due to the deepening of the mixed-layer (Table 3), and reduced biological activity (Metzl et al., 2006). This region also displays east/west differences in vertical mixing, the winter mixed layer being generally deeper to the east (Dong et al. 2008; Sallée et al., 2010), while our estimates of mixed layer depth suggest a stronger mixing during summer in the Agulhas Current region (down to $\sim 50 \text{ m}$ west of 60°E) than around 70°E (generally less than 30 m).

3.2.3. Frontal zone (40°S – 50°S). In the Southern Indian Ocean, the frontal zone includes three major fronts, the SSTF, the SAF and the PF. This singular hydrological structure brings nutrients to the surface layers therefore increasing primary production during summer and during winter (Figs 2 and 3). The frontal region is considered as one of the most pronounced sink for atmospheric CO_2 (Metzl et al. 1999; Takahashi et al., 2009). However, the ocean CO_2 sink is highly variable in this region especially during summer (Jabaud-Jan et al., 2004); this is related to mesoscale structure in (i) temperature and salinity (fronts and meanders) and (ii) biological activity that clearly impacts

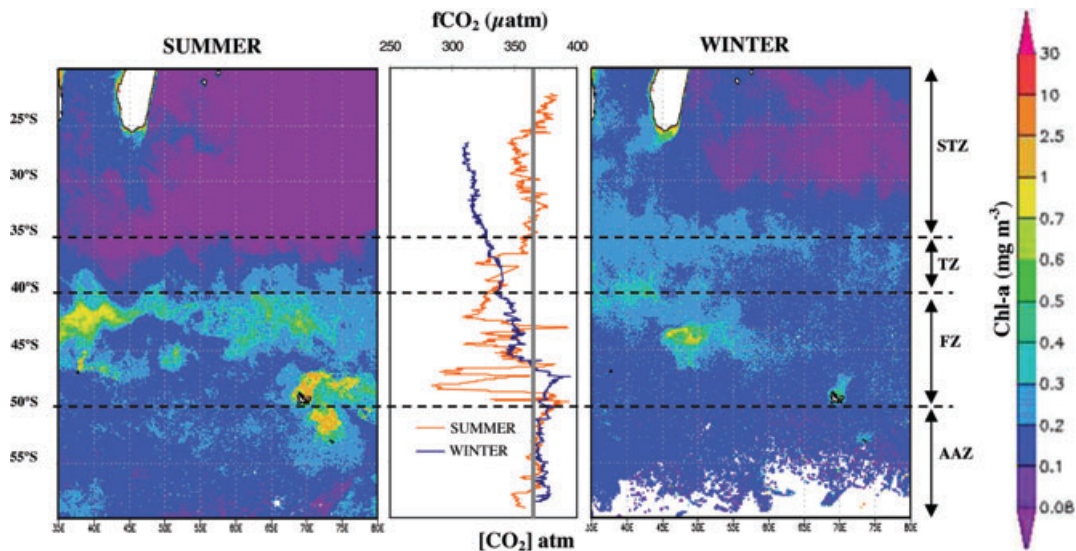


Fig. 2. Seasonal chlorophyll-a (SeaWiF map generated by Nasa's Giovanni, Giovanni.gsfc.nasa.gov; monthly composite with a spatial resolution of 9 km) and surface $f\text{CO}_2$ distribution (OISO data) in surface waters of Southwest Indian Ocean (summer 2002; winter 2000). **STZ**: subtropical zone; **TZ**: transition zone; **FZ**: frontal zone; **AAZ**: Antarctic zone.

on $f\text{CO}_2$ distribution (highs and lows, Fig. 2) and would likely affects $\delta^{13}\text{C}_{\text{DIC}}$ distribution in surface waters. In this paper, we divided this region into two subregions following the distribution of sea surface salinity (SSS; Table 2): the sub-Antarctic frontal zone (SAFZ; 40°S – 45°S), with a large SSS gradient and the polar frontal zone (PFZ; 45°S – 50°S),

3.2.4. Antarctic zone (South of 50°S). South of 50°S , in the Antarctic zone considered as a HNLC region (High-Nutrient Low-Chlorophyll; Fig. 3), surface $f\text{CO}_2$ is slightly higher in winter than in summer (Fig. 2). The seasonal variability of $f\text{CO}_2$ ($\sim 20 \mu\text{atm yr}^{-1}$) is much lower than in the subtropical and frontal zones. This is mainly due to biological activity during summer and vertical mixing in winter that dominate the thermodynamical effect during each season (Metzl et al., 2006; Metzl, 2009). These competing seasonal processes on $f\text{CO}_2$ and air–sea CO_2 fluxes would also impact on $\delta^{13}\text{C}_{\text{DIC}}$ distribution.

4. Method

4.1. Climatology of sea surface $\delta^{13}\text{C}_{\text{DIC}}$

The climatology of sea surface $\delta^{13}\text{C}_{\text{DIC}}$ was computed from OISO data collected between 1998 and 2005 (Table 1). The distribution of sea surface $\delta^{13}\text{C}_{\text{DIC}}$ is shown in Fig. 4 for summer and winter, indicating much higher variability in summer especially in the frontal zone (40°S – 50°S), that is also characterized by high variability in productivity (Fig. 2). Figure 4 also shows the mean surface $\delta^{13}\text{C}_{\text{DIC}}$ calculated in each region for summer and winter. This allows to identify three large negative anomalies ($\delta^{13}\text{C}_{\text{DIC}}$ lower than the mean): in summer 2002, particularly pronounced in the subtropical zone (Fig. 4a), in summer 2004

between 30°S and 40°S (Fig. 4a) and in winter 1998 in the polar frontal zone (Fig. 4b). These anomalies identified in Fig. 4 were not included in the climatology.

For austral summer (Fig. 4a) we have also plotted $\delta^{13}\text{C}_{\text{DIC}}$ measured in 1978 in the same region (GEOSECS data, Kroopnick, 1985) to show the clear decrease of $\delta^{13}\text{C}_{\text{DIC}}$ in the last decades, probably due to the invasion of anthropogenic CO_2 in the ocean, the so-called oceanic Suess Effect. Similarly, one can expect a decrease in surface $\delta^{13}\text{C}_{\text{DIC}}$ between 1998 and 2005, of the order of 0.1‰ (e.g. Gruber et al., 1999; Sonnerup et al., 2000; McNeil et al., 2001). For this reason the climatology is referenced to the year 2002 by correcting the observed $\delta^{13}\text{C}_{\text{DIC}}$ according to eq. (2).

$$\delta^{13}\text{C}_{\text{DIC}}^{\text{clim}} = \delta^{13}\text{C}_{\text{DIC}}^{\text{obs}} - (T^{\text{clim}} - T^{\text{obs}}) * 0.017, \quad (2)$$

where T^{clim} is the reference year and T^{obs} is the year of observation. The annual rate of $\delta^{13}\text{C}_{\text{DIC}}$ decrease is evaluated to $-0.017 \pm 0.009\text{‰ yr}^{-1}$ based on the OISO summer data collected between 1998 and 2005 (excluding data from the Mozambique channel). We did not include winter data to avoid introducing a seasonal bias, and we did not attempt to evaluate the winter trend because winter data are not equally distributed in space. Consequently, the annual rate calculated from summer data was used to correct both summer and winter data. However, if one might not expect similar trends for summer and winter, they should not be dramatically different, as suggested by the growth rate of oceanic $f\text{CO}_2$ which was evaluated around $2 \mu\text{atm yr}^{-1}$ for summer and winter from data collected in the same region between 1991 and 2007 (Metzl, 2009). In addition, the reference year ($T^{\text{clim}} = 2002$) was chosen so that the correction and its associated

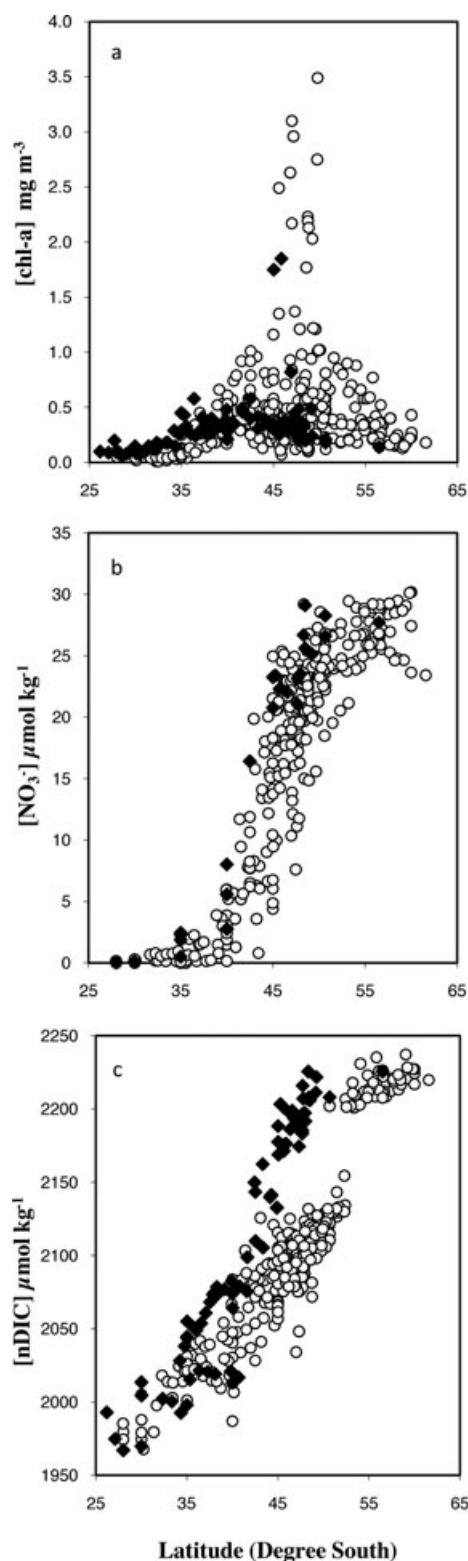


Fig. 3. Latitudinal distribution (a) in chlorophyll-a, (b) in Nitrate and (c) in DIC normalized in summer (white circles) and in winter (black diamonds) sampling during OISO cruises between 1998 and 2005.

uncertainty is minimized: the largest correction applied to the observed $\delta^{13}\text{C}_{\text{DIC}}$ is 0.05‰ (3 yr), but the average correction is between 0.01 and 0.02‰, which is of the same order than the standard deviation of $\delta^{13}\text{C}_{\text{DIC}}$ measurements. Finally, we did not correct $\delta^{13}\text{C}_{\text{DIC}}$ for the decrease in sea surface temperature observed in this region in recent years ($-0.11 \pm 0.03 \text{ }^{\circ}\text{C yr}^{-1}$; Metzl, 2009), because the isotopic fractionation effect due to temperature is very small ($0.105\text{‰ }^{\circ}\text{C}^{-1}$ according to Zhang et al. (1995)).

4.2. Physical effect versus biological effect: estimates of $\delta^{13}\text{C}^*$, $\Delta\delta^{13}\text{C}_{\text{bio}}$ and $\delta^{13}\text{C}_{\text{eq}}$

Following Gruber et al. (1999), we estimated two tracers, $\delta^{13}\text{C}^*$ and $\Delta\delta^{13}\text{C}_{\text{bio}}$, to identify the major process(es) controlling the distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in surface waters. This qualitative method assumes that air–sea exchange and biological activity are the only processes controlling the concentration of dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}\text{C}_{\text{DIC}}$), as expressed in the following mixing equation (Mook et al., 1983)

$$\text{DIC}(\delta^{13}\text{C}_{\text{DIC}}) = \Delta\text{DIC}_{\text{bio}}(\Delta\delta^{13}\text{C}_{\text{bio}}) + \text{C}^*(\delta^{13}\text{C}^*), \quad (3)$$

where C^* was described by Gruber et al. (1996) as the change in DIC concentration due to air–sea gas exchange only; $\Delta\text{DIC}_{\text{bio}}$ and $\Delta\delta^{13}\text{C}_{\text{bio}}$ represent the changes in DIC concentration and the change in the isotopic composition of DIC, respectively, due to biological activity, and $\delta^{13}\text{C}^*$ is the change in the isotopic composition of DIC resulting from air–sea gas exchange.

Regarding the biological effect, Gruber et al. (1999) differentiated between the soft-tissue pump (photosynthesis/respiration/remineralization) and the carbonate pump (formation/dissolution of calcium carbonate), giving the following equation for $\Delta\text{DIC}_{\text{bio}}$:

$$\Delta\text{DIC}_{\text{bio}} = \Delta\text{DIC}_{\text{org}} + \Delta\text{DIC}_{\text{carb}}, \quad (4)$$

where $\Delta\text{DIC}_{\text{org}}$ and $\Delta\text{DIC}_{\text{carb}}$ are the changes in DIC concentration due to the soft-tissue pump and the carbonate pump, respectively. Gruber et al. (1999) removed the contribution of the soft-tissue pump on DIC by using the change in phosphate as an indicator of biological activity. Since phosphate was not measured during the OISO cruises, here we used nitrate instead. The change in nitrate ($\Delta\text{NO}_3 = \text{NO}_3 - \text{NO}_3^{\circ}$) was converted into a change in DIC by assuming a constant ratio between carbon and nitrogen transferred during photosynthesis and respiration ($r_{\text{C:N}} = 117:16$, Anderson and Sarmiento, 1995). The contribution of the carbonate pump on DIC was removed by using the changes in nitrate and alkalinity ($\Delta\text{Alk} = \text{Alk} - \text{Alk}^{\circ}$). Equation (4) can therefore be expressed as follows:

$$\begin{aligned} \Delta\text{DIC}_{\text{bio}} = & r_{\text{C:N}}(\text{NO}_3 - \text{NO}_3^{\circ}) \\ & + 0.5(\text{Alk} - \text{Alk}^{\circ} + \text{NO}_3 - \text{NO}_3^{\circ}), \end{aligned} \quad (5)$$

Table 3. Summer and winter mean mixed-layer depth (MLD in metre—based on the layer where biogeochemical properties are homogeneous, notably DIC) and $\delta^{13}\text{C}_{\text{DIC}}$ (‰ vs V-PDB- corrected data—see text) associated to $\delta^{13}\text{C}^*$ and $\Delta\delta^{13}\text{C}_{\text{bio}}$ summer/winter change for STZ (subtropical zone), TZ (transition zone), SAFZ (sub-Antarctic frontal zone), PFZ (polar frontal zone) and AAZ (Antarctic zone). Between bracket, number of measurements that were used to calculate the mean MLD or $\delta^{13}\text{C}_{\text{DIC}}$.

	Summer	Winter	Summer	Winter	Summer – winter	
	MLD (m)	MLD (m)	$\delta^{13}\text{C}_{\text{DIC}}^{\text{clim}}$ (‰)	$\delta^{13}\text{C}_{\text{DIC}}^{\text{clim}}$ (‰)	$\Delta\delta^{13}\text{C}^*$ (‰)	$\Delta\delta^{13}\text{C}_{\text{bio}}$ (‰)
STZ	20 ± 10 (22)	117 ± 45 (9)	1.1 ± 0.08 (30)	0.95 ± 0.08 (29)	0.08	0.02
TZ	31 ± 22 (15)	280 ± 214 (4)	1.41 ± 0.11 (31)	1.14 ± 0.08 (19)	0.13	0.16
SAFZ	42 ± 31 (16)	125 ± 43 (3)	1.61 ± 0.17 (33)	1.42 ± 0.12 (18)	−0.76	0.89
PFZ	66 ± 30 (46)	165 ± 34 (10)	1.66 ± 0.20 (161)	1.58 ± 0.12 (14)	−0.06	0.18
AAZ	88 ± 38 (8)	150 ± 0 (2)	1.36 ± 0.11 (55)	1.26 (1)	0	0.07

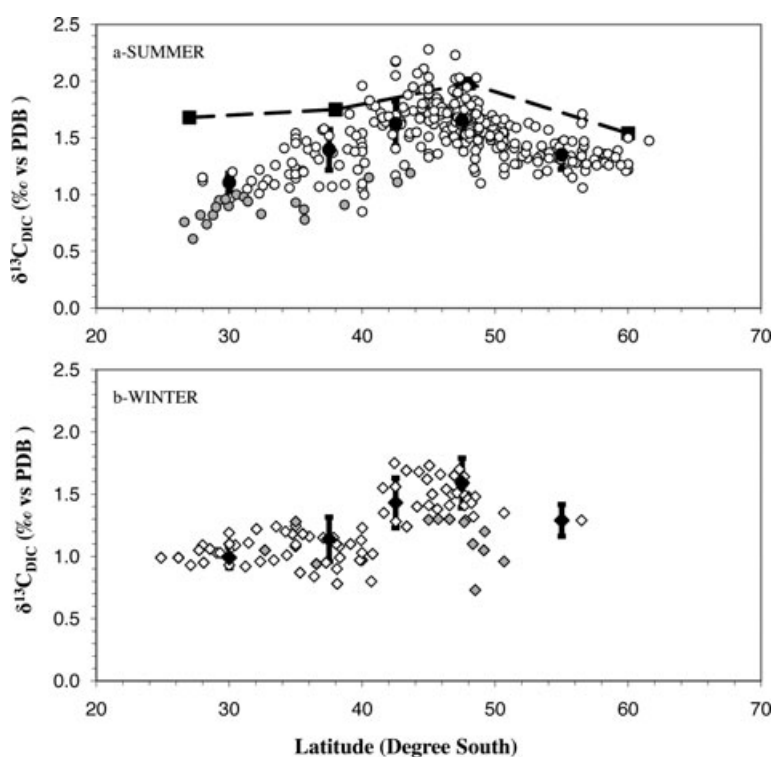


Fig. 4. Latitudinal distribution of sea surface $\delta^{13}\text{C}_{\text{DIC}}$ in Southwest Indian Ocean during summer (a) and during winter (b). Black squares: GEOSECS data, 1978 (Kroopnick, 1985); white circles: OISO summer data (1998–2005); white diamonds: OISO winter data (1998–2002); black circles and diamonds: regional average with their standard deviation; grey circles and diamonds: OISO data anomalies.

where NO_3° and Alk° are constant reference values (Gruber et al., 1999). Based on eqs (3) and (5), Gruber et al. (1999) demonstrated that $\delta^{13}\text{C}^*$ can be calculated as follows:

$$\delta^{13}\text{C}^* = \text{DIC}/\text{C}^* \times [\delta^{13}\text{C} - (r_{\text{C:n}}\delta^{13}\text{C}_{\text{org}}\Delta\text{NO}_3)/\text{DIC} - \delta^{13}\text{C}_{\text{carb}}(\Delta\text{Alk} + \Delta\text{NO}_3)/2\text{DIC}]. \quad (6)$$

We computed $\delta^{13}\text{C}^*$ from OISO data, with DIC and Alk normalized to a constant salinity of 35 to remove evaporation and precipitation effects. To compare our results to those obtained by Gruber et al. (1999), we adopted the same constants and reference values: we assume values of 1 for DIC/C^* , 2‰ for $\delta^{13}\text{C}_{\text{carb}}$, −20‰ for $\delta^{13}\text{C}_{\text{org}}$, 0 $\mu\text{mol kg}^{-1}$ for NO_3° and 2310 $\mu\text{mol kg}^{-1}$ for Alk° . Because $\delta^{13}\text{C}^*$ was defined as the difference between

the observed $\delta^{13}\text{C}$ and the biological signature ($\Delta\delta^{13}\text{C}_{\text{bio}}$), and since the distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in surface waters is controlled by air–sea gas exchange, biological activity and ocean dynamics (McNeil et al., 2001; Tagliabue and Bopp, 2008), we will refer to $\delta^{13}\text{C}^*$ as ‘the physical signature’, a general term including both air–sea gas exchange and ocean dynamics.

The distribution of $\delta^{13}\text{C}^*$ in the Southwest Indian Ocean is presented in the following section, together with the biological signature ($\Delta\delta^{13}\text{C}_{\text{bio}} = \delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}^*$). To help in the interpretation of $\delta^{13}\text{C}^*$, we also computed a third tracer, $\delta^{13}\text{C}_{\text{eq}}$, defined as the isotopic composition of the dissolved inorganic carbon if the ocean and the atmosphere were in isotopic equilibrium. $\delta^{13}\text{C}_{\text{eq}}$ was described and formulated by Mook (1986) following

eqs (7) and 8, where the isotopic enrichment factor (ϵ) depends on the sea surface temperature ($^{\circ}\text{Kelvin}$) and where the atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ was estimated to -7.74‰ in 1988 and decreased by about 0.02‰ yr^{-1} on average

$$\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{CO}_2} \text{ g} - \epsilon^{13}\text{C}_{\text{CO}_2-\text{DIC}} \quad (7)$$

$$\epsilon^{13}\text{C}_{\text{CO}_2-\text{DIC}} = -9483 \cdot T^{-1} + 23.9. \quad (8)$$

5. Surface distribution of $\delta^{13}\text{C}$ of DIC in the South Indian Ocean

5.1. Summer $\delta^{13}\text{C}_{\text{DIC}}$ distribution

In the Southwest Indian Ocean, the maximum surface $\delta^{13}\text{C}_{\text{DIC}}$ ($>1.8\text{‰}$) was detected in the frontal zone (40°S – 50°S), North of Kerguelen and Crozet Islands (Fig. 5a). Low $\delta^{13}\text{C}_{\text{DIC}}$ ($<1.0\text{‰}$) was observed in the subtropical region (25°S – 35°S , Figs 4a and 5a). The lowest $\delta^{13}\text{C}_{\text{DIC}}$ ($<0.8\text{‰}$) was found in the Mozambique channel sampled in austral summer 2004 only (Fig. 5a). The meridional increase of surface $\delta^{13}\text{C}_{\text{DIC}}$ was associated with an increase in chl-a concentrations from the subtropics to the frontal zone (Figs 2 and 3a), suggesting that biological activity was the main driver for the summer distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in these regions: as phytoplankton preferentially uses ^{12}C during photosynthesis, the increase in primary production causes the increase of the $\delta^{13}\text{C}_{\text{DIC}}$ values in surface waters. North of

the frontal zone (40°S – 45°S), the $\delta^{13}\text{C}_{\text{DIC}}$ values and chl-a concentrations are higher ($1.75 \pm 0.11\text{‰}$ around 45°E – 55°E) in the western region than in the eastern region ($1.56 \pm 0.16\text{‰}$ around 70°E – 80°E). In Antarctic waters, South of the Polar front ($\sim 50^{\circ}\text{S}$), the climatology shows lower $\delta^{13}\text{C}_{\text{DIC}}$ values ($1.36 \pm 0.11\text{‰}$), associated with moderate summer primary production (Figs 2 and 3a) and $f\text{CO}_2$ near equilibrium (Fig. 2).

5.2. Winter $\delta^{13}\text{C}_{\text{DIC}}$ distribution

The winter climatology of $\delta^{13}\text{C}_{\text{DIC}}$ shows similar meridional and zonal distributions as during summer, but surface gradients are much less pronounced (Figs 4b and 5b). Similarly as during summer, maximum $\delta^{13}\text{C}_{\text{DIC}}$ values ($>1.7\text{‰}$) were observed in the frontal zone (40°S – 50°S) and low values ($\sim 1\text{‰}$) were measured North of 40°S (STZ and TZ regions). Very low $\delta^{13}\text{C}_{\text{DIC}}$ were also identified at local scale, around 40°S ($< 0.8\text{‰}$, Fig. 3b), associated with the deepest mixed layer (150 – 500 m). In the subtropics, $\delta^{13}\text{C}_{\text{DIC}}$ values were slightly lower in the western region ($0.95 \pm 0.08\text{‰}$) than in the eastern region ($1.12 \pm 0.07\text{‰}$). In the frontal zone, where $\delta^{13}\text{C}_{\text{DIC}}$ values range from 1.30 to 1.76‰ , the persistence of biological activity during winter must play a major role in the control of surface $\delta^{13}\text{C}_{\text{DIC}}$. Conversely to the subtropics, $\delta^{13}\text{C}_{\text{DIC}}$ was higher in the western frontal region than in the eastern frontal region, which can be explained by stronger biological activity to the west, as revealed by satellite observations (Fig. 2).

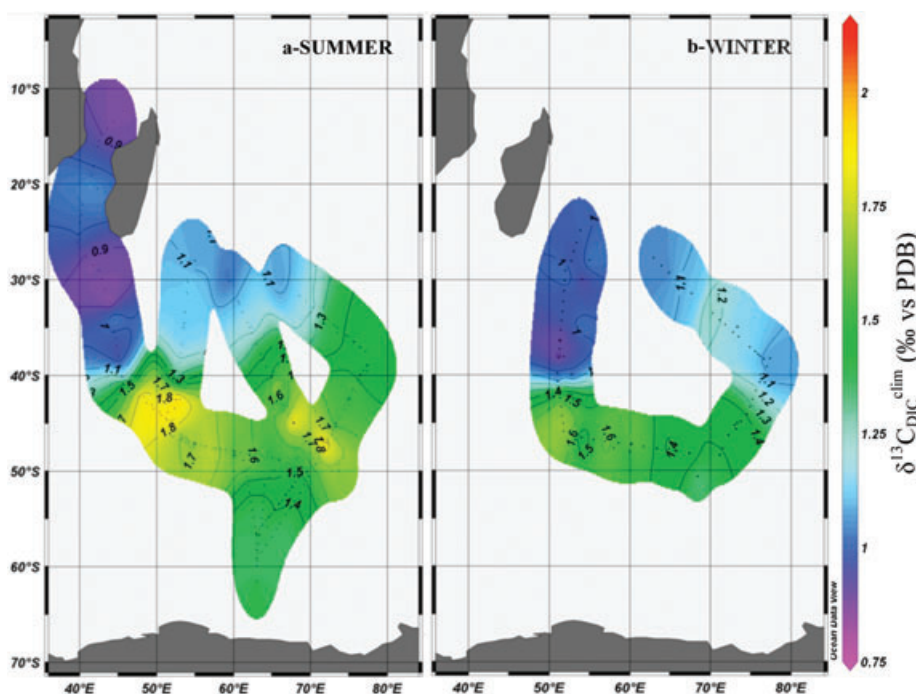


Fig. 5. Seasonal climatology of sea surface $\delta^{13}\text{C}_{\text{DIC}}$ in the Southwest Indian Ocean (20°S – 60°S). Each value (black dots) are referenced to the year 2002 by correcting surface $\delta^{13}\text{C}_{\text{DIC}}$ by -0.017‰ yr^{-1} . Summer = Jan/Feb; Winter = Jul/Aug/Sept (ODV gridding interpolation; Schlitzer, 2002).

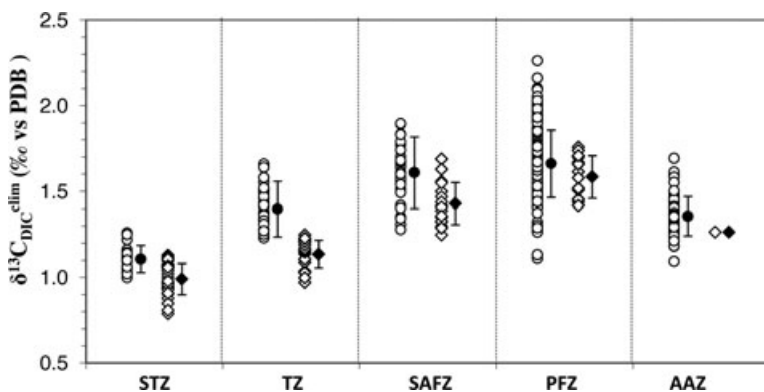


Fig. 6. Zonal distribution of sea surface $\delta^{13}\text{C}_{\text{DIC}}$ (corrected OISO data—see text) in summer (white circles) and in winter (white diamonds) with their average (black dots) and standard deviation (black lines) for each region. STZ: subtropical zone; TZ: transition zone; SAFZ: sub-Antarctic frontal zone; PFZ: polar frontal zone; AAZ: Antarctic zone.

6. Summer/winter variations

Figure 6 and Table 3 synthesize the summer/winter variations of surface $\delta^{13}\text{C}_{\text{DIC}}$ observed in the South Indian Ocean. At all latitudes, from 20°S to 60°S , $\delta^{13}\text{C}_{\text{DIC}}$ was on average higher during summer than during winter. The largest summer/winter change ($\sim 0.3\text{‰}$) was detected in the transition region (TZ, 35°S – 40°S). This is lower than the summer/winter change observed in the frontal zone South of Tasmania over the period 1997–1999 ($\sim 0.45\text{‰}$; McNeil and Tilbrook, 2009). In the latter study, the authors attribute the summer/winter variations to both biological activity that is responsible for high $\delta^{13}\text{C}_{\text{DIC}}$ during summer, and vertical mixing that brings ‘light’ DIC (low $\delta^{13}\text{C}_{\text{DIC}}$) to surface waters during winter, in good agreements with our observations. It is likely that the larger summer/winter change is due to strong winter mixing generally observed in the eastern Indian Ocean (Dong et al., 2008; Sallée et al., 2010a, b). In the sub-Antarctic frontal zone (40°S – 50°S), the seasonal change of surface $\delta^{13}\text{C}_{\text{DIC}}$ is about 0.2‰ (Table 3, Fig. 6), much less pronounced than in the TZ. The summer/winter variation is even smaller in the Polar Frontal Zone ($\sim 0.1\text{‰}$) and not always clearly detected, as also reported by McNeil and Tilbrook (2009) for the eastern Indian sector. South of the Polar Front ($>50^{\circ}\text{S}$), in the cold HNLC ocean, the average $\delta^{13}\text{C}_{\text{DIC}}$ in summer is clearly lower than in the frontal zone (Table 3, Fig. 6); in winter, the single data available south of 50°S also suggests lower $\delta^{13}\text{C}_{\text{DIC}}$ at higher latitudes. North of 35°S , in the subtropical zone, the mean summer/winter amplitude in $\delta^{13}\text{C}_{\text{DIC}}$ is clearly detected ($\sim 0.15\text{‰}$). In this region the summer/winter variations of surface $\delta^{13}\text{C}_{\text{DIC}}$ can be attributed to air–sea CO_2 fluxes that increase from summer (near equilibrium) to winter (uptake of CO_2) (Fig. 2; Metzl et al., 2006) and the deepening of the mixed layer from 30 m or less during summer to 50–150 m during winter (Table 3). The average summer/winter change observed in the subtropical Indian Ocean is about half that observed in other subtropical regions. In the North Atlantic, based on $\delta^{13}\text{C}_{\text{DIC}}$ time-series at BATS, Gruber and Keeling (1999) and Gruber et al. (1998, 1999), showed that about half of the seasonal variability (0.2 – 0.3‰) observed in the subtropical zone resulted from summer primary

production, and half was due to the combined effect of air–sea CO_2 fluxes and vertical mixing. Interannual change of any of these processes could impact on the $\delta^{13}\text{C}_{\text{DIC}}$ distribution.

7. Biological and physical signatures

The surface $\delta^{13}\text{C}_{\text{DIC}}$ is rarely in isotopic equilibrium with atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ (Broecker and Peng, 1982) because the residence time of the surface water (~ 1 yr) is shorter than the time needed for CO_2 to reach isotopic equilibrium with the atmosphere (~ 10 yr, Broecker and Peng, 1974; Lynch-Stieglitz et al., 1995; Gruber et al., 1999). Indeed, Fig. 7 shows that the observed $\delta^{13}\text{C}_{\text{DIC}}$ are higher than $\delta^{13}\text{C}_{\text{eq}}$ at mid-latitudes (North of 45°S during summer and 35°S during winter), whereas they are lower than $\delta^{13}\text{C}_{\text{eq}}$ in the Antarctic zone during both summer and winter. Isotopic disequilibrium, which is the difference between $\delta^{13}\text{C}_{\text{eq}}$ and the observed $\delta^{13}\text{C}_{\text{DIC}}$ is accentuated by the impact of biological activity and ocean dynamics on $\delta^{13}\text{C}_{\text{DIC}}$ whose response is quicker than ocean–atmosphere isotopic equilibration. Surface $\delta^{13}\text{C}_{\text{DIC}}$ appears to be close to isotopic equilibrium with atmospheric CO_2 around 45°S during summer and from 35°S to 40°S during winter ($\delta^{13}\text{C}_{\text{eq}} = \delta^{13}\text{C}_{\text{DIC}}$), but this is more likely the result of the compensation between the biological and physical effects.

The distribution of surface $\delta^{13}\text{C}^*$ and $\Delta\delta^{13}\text{C}_{\text{bio}}$ between 25°S and 65°S during summer and during winter allows to discriminate between the physical and biological processes that are responsible for the $\delta^{13}\text{C}_{\text{DIC}}$ variations (Fig. 8). In the subtropical zone $\delta^{13}\text{C}^*$ was equal to the observed $\delta^{13}\text{C}_{\text{DIC}}$ during both seasons, suggesting that physical processes only controlled the distribution of surface $\delta^{13}\text{C}_{\text{DIC}}$. At seasonal scale, changes in sea surface temperature can substantially affect $\delta^{13}\text{C}_{\text{DIC}}$ in this region: assuming isotopic equilibrium with atmospheric CO_2 , a mean warming of 6°C (Table 2) would decrease $\delta^{13}\text{C}_{\text{DIC}}$ by 0.6‰ (Zhang et al., 1995). This suggests that the small increase in $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}^*$ between winter and summer (0.15 and 0.08‰ , respectively, Table 3) would result from the opposite effects of the changes in sea surface pCO_2 (dominant) and

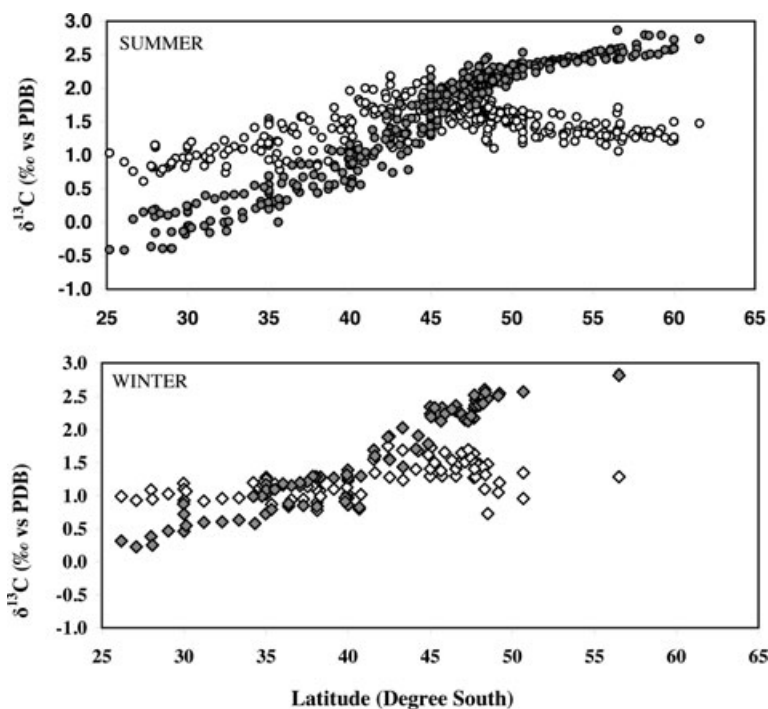


Fig. 7. Meridional distribution of $\delta^{13}\text{C}_{\text{eq}}$ (dark grey circles and diamonds) and $\delta^{13}\text{C}_{\text{DIC}}$ (no corrected data—see text) sampling during OISO cruises between 1998 and 2005 during summer (white circles) and during winter (white diamonds).

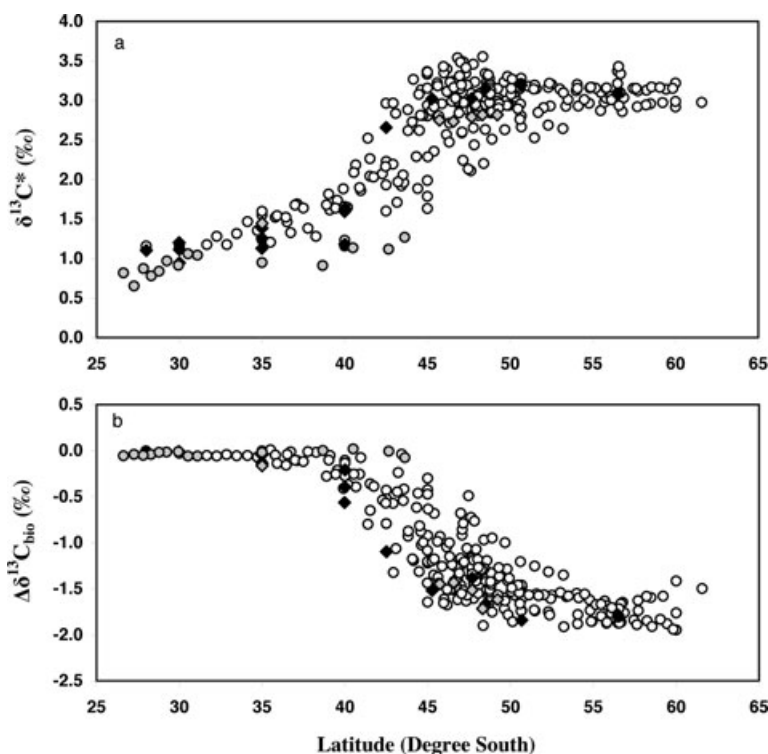


Fig. 8. Meridional distribution of (a) $\delta^{13}\text{C}^*$ and (b) $\Delta\delta^{13}\text{C}_{\text{bio}}$ estimated for South Indian Ocean in summer (white circles) and in winter (black diamonds). Grey circles and diamonds symbolize $\delta^{13}\text{C}_{\text{DIC}}$ anomalies.

temperature. Previous studies and observations also showed the deepening of the mixed layer during winter in the subtropical zone (Metzl et al., 1998; Table 3), which should increase nutrients in the surface layer and therefore enhance photosynthesis resulting in the increase of $\delta^{13}\text{C}_{\text{DIC}}$. However, winter mixing

also brings ‘light’ DIC to the surface (low $\Delta\delta^{13}\text{C}_{\text{bio}}$), which can explain why we did not find any substantial summer/winter variation in the biological signature (Table 3).

Farther south, in the frontal region (40°S–50°S), we observe a large variability in $\Delta\delta^{13}\text{C}_{\text{bio}}$ and $\delta^{13}\text{C}^*$ values (Fig. 8), as also

observed for the distribution of $\delta^{13}\text{C}_{\text{DIC}}$ in this region (Fig. 4). Here, $\delta^{13}\text{C}^*$ increases southward to reach a maximum value of 3.5‰ between 45°S and 50°S (Fig. 8a), that is lower by 0.5‰ than the $\delta^{13}\text{C}^*$ calculated by Gruber et al. (1999) from data collected in the same region in 1978 and 1985. The southward increase of $\delta^{13}\text{C}^*$ suggests that physical processes (air–sea gas exchange due to sea surface cooling and/or ocean circulation) would have a stronger influence south of the frontal zone than in the subtropics. This is shown by the biological signature given by the $\Delta\delta^{13}\text{C}_{\text{bio}}$ values that decrease by 2‰ between 40°S and 50°S (Fig. 8b); a similar decrease was reported by Gruber et al. (1999) based on the data set of years 1978 and 1985. According to eqs (5) and (6), and since ΔAlk is close to zero, the decrease southward of $\Delta\delta^{13}\text{C}_{\text{bio}}$ is strongly linked to the increase in nitrate concentrations (Fig. 3b): the upwelling of old, nitrate-rich waters, also brings ‘light’ DIC to the surface (low $\Delta\delta^{13}\text{C}_{\text{bio}}$), while nutrient utilization by photosynthesis is associated with an increase in $\delta^{13}\text{C}_{\text{DIC}}$ (maximum chl-a and $\delta^{13}\text{C}_{\text{DIC}}$ at 45°S, Figs 3a and 7). However, if enhanced biological activity in the frontal zone suggests a large potential change in $\delta^{13}\text{C}_{\text{DIC}}$, it is also the driving force for the uptake of atmospheric CO_2 , which acts against photosynthesis by decreasing $\delta^{13}\text{C}_{\text{DIC}}$. In this region, the balance between physical and biological effects is also observed at seasonal scale (Table 3): $\Delta\delta^{13}\text{C}_{\text{bio}}$ increases with photosynthesis from winter to summer, and $\delta^{13}\text{C}^*$ decreases with the increase of CO_2 uptake (Fig. 2; Metzl et al., 2006). The largest potential changes of $\delta^{13}\text{C}_{\text{DIC}}$ that can be induced by biological activity and air–sea CO_2 fluxes are found in the sub-Antarctic Frontal zone, but the effective change is small (0.2‰). In the Transition zone and in the Polar Frontal zone, the winter to summer change in the biological signature (variation of $\Delta\delta^{13}\text{C}_{\text{bio}}$ of about 0.2‰) is similar to that estimated by McNeil and Tillbrook (2009) based on observations collected South of Australia.

South of the Polar front, in the High Nutrient Low Chlorophyll (HNLC) region (Figs 3a and b), we estimated the maximum $\delta^{13}\text{C}^*$ (Fig. 8a) associated with the minimum $\Delta\delta^{13}\text{C}_{\text{bio}}$ (Fig. 8b). This again shows the large potential changes of $\delta^{13}\text{C}_{\text{DIC}}$ that can be induced by biological activity and air–sea CO_2 fluxes, despite small changes in the observed $\delta^{13}\text{C}_{\text{DIC}}$ (Fig. 7): Antarctic surface waters are strongly influenced by the upwelling of deep waters that brings ‘old’ DIC in the surface layer, and leads to two competing effects on the surface $\delta^{13}\text{C}_{\text{DIC}}$, a low $\Delta\delta^{13}\text{C}_{\text{bio}}$ reflecting remineralization processes (Gruber et al., 1999) and a high $\delta^{13}\text{C}^*$ indicating an ‘older’ atmospheric imprint (atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ higher than today; Tagliabue and Bopp, 2008). In this region, the winter to summer changes in $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}^*$ and $\Delta\delta^{13}\text{C}_{\text{bio}}$ (Table 3) suggest that the small increase in $\delta^{13}\text{C}_{\text{DIC}}$ (0.1‰) would be mainly due to photosynthesis.

On interannual scale, we have detected two large negative anomalies in the distribution of $\delta^{13}\text{C}_{\text{DIC}}$. The first anomaly ($\delta^{13}\text{C}_{\text{DIC}} = 0.61\text{--}1.00\text{‰}$) was observed North of 35°S between La Réunion and Amsterdam Islands (26–32°S, 60–70°E, Fig. 4)

in February 2002. At this time, surface $f\text{CO}_2$ ($\sim 355\text{ }\mu\text{atm}$) was well below the atmospheric level ($>370\text{ }\mu\text{atm}$), although surface water CO_2 in this region is usually close to isotopic equilibrium with atmospheric CO_2 during summer (Fig. 9a). This large anomaly in oceanic $f\text{CO}_2$, that explains the low $\delta^{13}\text{C}_{\text{DIC}}$ values, is attributed to the low sea surface temperature (SST) measured during the cruise (Fig. 9b) and also clearly detected over a large region, as revealed by monthly maps of SST anomalies (SST was lower by 1.5°C at 25°S–35°S/50°E–90°E, <http://ingrid.ideo.columbia.edu/SOURCES/IGOSS/>). This event, a very cold period associated with a decrease in $f\text{CO}_2$, again points to both air–sea CO_2 fluxes and temperature changes as drivers for the surface $\delta^{13}\text{C}_{\text{DIC}}$ variability observed in the subtropical zone. The second anomaly was detected in the frontal zone during winter 1998. The analysis of water column data revealed deeper mixed layers in 1998 than other years, but further analysis are needed to firmly conclude on others potential contributors.

8. Summary and conclusion

In this study, we described new surface water $\delta^{13}\text{C}_{\text{DIC}}$ observations obtained during summer and winter in the Southwestern Indian Ocean (25°S–60°S) over the period 1998–2005 (10 OISO cruises, $\sim 370\text{ }\delta^{13}\text{C}_{\text{DIC}}$ samples). These new observations represent an important complement to previous cruises conducted in the late 1970s, 1980s and 1990s during GEOSECS, INDIGO and WOCE expeditions (Gruber et al., 1999; Sonnerup et al., 2000; Key et al., 2004). In the OISO data set, the $\delta^{13}\text{C}_{\text{DIC}}$ ranged between 0.77‰ and 2.26‰. This highlights both spatial and temporal variabilities of $\delta^{13}\text{C}_{\text{DIC}}$ which are controlled by the complex coupling of processes, biological activity (production/remineralization), vertical mixing and air–sea gas exchanges.

The minimum of 0.77‰ was observed during austral summer (in 2004) in the Mozambic Channel; to our knowledge these are the first $\delta^{13}\text{C}_{\text{DIC}}$ data ever obtained in this region. Remarkably, the $\delta^{13}\text{C}_{\text{DIC}}$ in the Mozambic Channel are much lower than any previous $\delta^{13}\text{C}_{\text{DIC}}$ data reported in the tropical zone of the oceans (excepted in the vicinity of the Congo River in the eastern tropical Atlantic, Vangriesheim et al., 2009). This is also very low compared to $\delta^{13}\text{C}_{\text{DIC}}$ simulated in this region (Tagliabue and Bopp, 2008). The maximum of 2.26‰ was also observed in summer (2001) in the sub-Antarctic zone (North of Crozet Islands) that experienced high productivity during this season. This maximum is very high compared to previous $\delta^{13}\text{C}_{\text{DIC}}$ reported or simulated in the circumpolar sub-Antarctic zone (Gruber et al., 1999; Tagliabue and Bopp, 2008; McNeil and Tillbrook, 2009). Given that sea surface $\delta^{13}\text{C}_{\text{DIC}}$ present so large deviations between regions and years, we have averaged a selection of summer and winter data over 8 yr to investigate the mean changes between summer and winter.

At all latitudes, $\delta^{13}\text{C}_{\text{DIC}}$ was on average higher during austral summer than during winter. In the subtropical oligotrophic

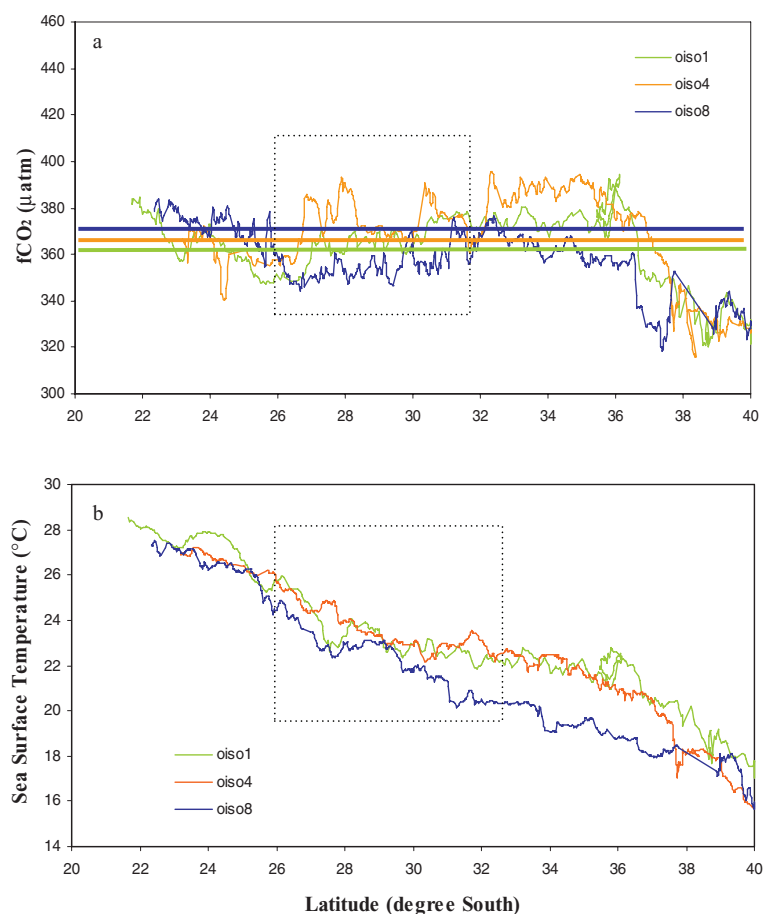


Fig. 9. Distribution of (a) sea surface $f\text{CO}_2$ and (b) temperature during summer 1998 (green), 2000 (orange) and 2002 (blue) in the subtropical zone between La Réunion and Amsterdam (26°S – 32°S , 60°E – 70°E) with atmospheric CO_2 concentration for each year (horizontal lines). Anomaly zone is characterized with a large open square.

waters the mean winter-to-summer change in $\delta^{13}\text{C}_{\text{DIC}}$ was $\sim 0.15\text{‰}$, and attributed to the large ocean CO_2 sink observed during winter and near equilibrium with atmospheric CO_2 during summer. South of the subtropical zone, in the region 35°S – 40°S we observed the largest summer-winter changes in $\delta^{13}\text{C}_{\text{DIC}}$ ($\sim 0.3\text{‰}$) associated to the largest deepening of the mixed layer (e.g. Table 3); this $\delta^{13}\text{C}_{\text{DIC}}$ change is attributed to contrasting seasonal processes, biological activity (photosynthesis) during summer and deep mixing and CO_2 uptake during winter. In the frontal region between 40°S and 50°S , the maximum $\delta^{13}\text{C}_{\text{DIC}}$ ($> 2\text{‰}$) was also observed in austral summer and mainly due to enhanced biological activity. However, the variability of biological activity in the Frontal Zone imprinted a large range of $\delta^{13}\text{C}_{\text{DIC}}$ values (1.1 – 2.3‰) depending the year and locations, leading to less firm conclusions regarding the seasonal signal. South of the Polar Front, in the cold Antarctic waters, we also observed a decrease of $\delta^{13}\text{C}_{\text{DIC}}$ from summer to winter, that could be also explained by higher productivity in summer and deep mixing in winter, but this conclusion is based on very few data during austral winter.

Nevertheless, this summer/winter $\delta^{13}\text{C}_{\text{DIC}}$ climatology constructed in the South Indian Ocean (25°S – 60°S) represents a new basis for studying $\delta^{13}\text{C}_{\text{DIC}}$ interannual variability as well as

for better evaluating the anthropogenic component of the CO_2 in the ocean (e.g. Fig. 4a). The data could also add important new constraints for atmospheric inversed transport models, as well as new fields to better evaluate the seasonal variation of $\delta^{13}\text{C}_{\text{DIC}}$ in ocean models (Tagliabue and Bopp, 2008).

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