

# Atmospheric CO<sub>2</sub> concentrations and $\delta^{13}\text{C}$ values between New Zealand and Antarctica, 1998 to 2010: some puzzling results

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## ABSTRACT

From 1998 to 2010, during eight cruises of the M/V *Italica* between New Zealand and Antarctica, sets of flask air samples were collected and atmospheric CO<sub>2</sub> concentrations were recorded. The  $\delta^{13}\text{C}$  of CO<sub>2</sub> from the 1998 to 2003 air samples have already been published and show large interannual variability and an increasing frequency of <sup>13</sup>C-depleted samples. These results were related to a mosaic of areas with positive air–sea fluxes. We report here  $\delta^{13}\text{C}$  results from air samples collected from four further cruises.  $\delta^{13}\text{C}$  values obtained during the 2004/2005 cruise show an inexplicable saw-toothed distribution. Air samples from the 2005/2006 cruise have  $\delta^{13}\text{C}$  values which match previous sets of samples (1998 to 2004) and show more frequent and more negative isotopic events. From 2006 until 2009, further samples could not be collected. However, during December 2009 and January 2010, two more sets of air samples were collected, the  $\delta^{13}\text{C}$  values of which greatly differ from previous results, being absolutely homogeneous and paralleled by flat CO<sub>2</sub> concentrations. The results of these last two sets of air samples may be due either to fortuitous environmental conditions or to an improbable and substantial change in oceanic and atmospheric conditions in this section of the circumpolar area.

**Keywords:** *New Zealand to Antarctica, flask air samples, atmospheric CO<sub>2</sub> concentrations, carbon isotopic composition of CO<sub>2</sub>, puzzling results*

## 1. Introduction

Every year, the oceans, which contain about 50 times more carbon (39 000 PgC) than the atmosphere, take up about 25% of anthropogenically produced carbon (IPCC, 2007). Net CO<sub>2</sub> transfer across the air–sea interface occurs whenever a partial pressure difference is established between atmosphere and ocean. The net flux (F) of CO<sub>2</sub> across the air–sea interface is given by the product of the differences in partial CO<sub>2</sub> pressure and a kinetic term (k), known as the transfer velocity (it has dimensions of length per time):

$$F = k s (p\text{CO}_{2\text{w}} - p\text{CO}_{2\text{a}})$$

where *s* is the CO<sub>2</sub> solubility coefficient and *p*CO<sub>2w</sub> and *p*CO<sub>2a</sub> are the partial pressures of CO<sub>2</sub> in water and air, respectively. Oceanic sinks and sources of CO<sub>2</sub> are then highly variable and sensitive to climate and local environmental conditions. Besides temperature and biological processes, fluxes are driven by several different processes, such as near-surface turbulence at moderate wind speed (Zappa et al., 2007) and the formation of air bubbles (Woolf, 1997). However, wind is the primary forcing of the aqueous boundary layer which controls gas exchange. Quantitative relationships between gas exchange and wind speed have been suggested by several authors (Liss and Merlivat, 1986; Wanninkhof, 1992; Wanninkhof and McGillis, 1999). Air–sea gas exchange models and theory were exhaustively reviewed by Nightingale (2009), who discussed a wide range of processes from chemical biological enhancement, the surface renewal model, the

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surface penetration theory, the turbulence dissipation rate, the bubble-mediated gas transfer, the role of wave breaking, and so on.

During the last two decades, several authors have shown that the Southern Oceans and, in particular, the Circumpolar Antarctic and sub-Antarctic zones behave not only as sinks but also as sources of  $\text{CO}_2$ , according to changing environmental conditions (Takahashi et al., 1993, 1997, 2002, 2009; Hoppema et al., 1995, 1999, 2000; Bakker et al., 1997; Metzl et al., 1999; De Baar and Boyd, 2000; Stoll et al., 2002). In these authors' views, temperature is a very important factor affecting the air-sea exchange, although plankton blooms may sometimes be even more important. Roy et al. (2003) and Metzl et al. (2006) disputed the magnitude of the  $\text{CO}_2$  sink in that area and Le Quéré et al. (2007) estimated a weakening of the Southern Ocean sink between 1981 and 2004, attributing it to the observed increase in Southern Ocean winds in that period; Zickfeld et al. (2008) disagreed with these conclusions, and stated that, 'Ekman-driven upwelling in the Antarctic Divergence exposes deep waters with elevated concentrations of dissolved inorganic carbon (DIC) to the surface, leading to outgassing of natural  $\text{CO}_2$  to the atmosphere'.

With the only exception of three carbon isotope measurements reported by Inoue and Sugimura (1986), direct measurements of atmospheric  $\text{CO}_2$  concentrations and its carbon isotope values in the area between New Zealand and Antarctica had never been reported until a few years ago, when Longinelli et al. (2007) reported the  $\text{CO}_2$  concentrations, measured in that area in the course of three different cruises, together with the carbon isotope composition of atmospheric  $\text{CO}_2$  from discrete air samples collected in 4L Pyrex flasks during four cruises. These results showed 'several  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$

considerably lighter than the background values measured over the oceans'. These quite negative values, ranging from about  $-8.5$  to  $-10.3$  ‰ (vs. Vienna Pee-Dee-Belemnite VPDB standard), were tentatively related to 'partial contributions by different causes such as the southern negative gradient of  $\delta^{13}\text{C}_{\text{DIC}}$ , the upwelling of deep waters and their northward transport, subsurface mixing processes and, finally, the possible contribution of biological heterotrophic activity and the production of isotopically light  $\text{CO}_2$  by remineralization processes of decomposing planktonic organic matter' (Longinelli et al., 2007). Conclusions by several authors about the possibility of  $\text{CO}_2$  flowing from the ocean surface to the atmosphere in sections of the circumpolar Antarctic area agree with those by Longinelli et al. (2007) and with the reported  $\delta^{13}\text{C}$  values. It is quite difficult to state the precise relationships existing between the carbon isotope values of atmospheric  $\text{CO}_2$  and environmental conditions, which should be accurately monitored by research vessels. This was even more difficult in our case, since flask air samples represent instantaneous atmospheric conditions and were collected on board a cargo ship, where the lack of appropriate instrumentation prevented the collection of other data which would have been important in interpreting isotopic data. We report here atmospheric  $\text{CO}_2$  concentrations and  $\delta^{13}\text{C}$  values obtained from discrete air samples collected during four further cruises between New Zealand and Antarctica in 2004/2005, 2005/2006, 2009 and 2010, and compare them with previous data.

## 2. Analytical techniques

A Siemens Ultramat 5E analyser assembled for shipboard use (Ori et al., 1996; Lenaz et al., 2000; Longinelli et al.,

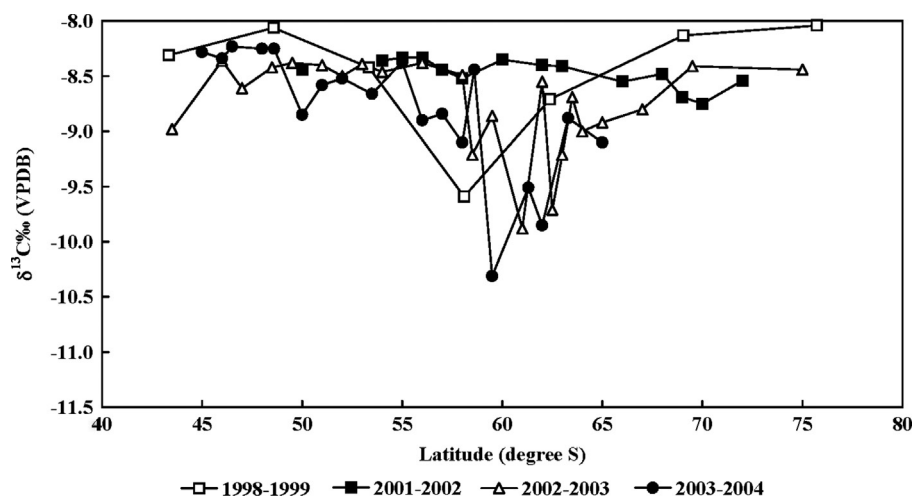


Fig. 1.  $\delta^{13}\text{C}$  values of the  $\text{CO}_2$  from discrete air samples collected between New Zealand and Antarctica during four cruises between 1998–1999 and 2003–2004. These results were already reported by Longinelli et al. (2007).

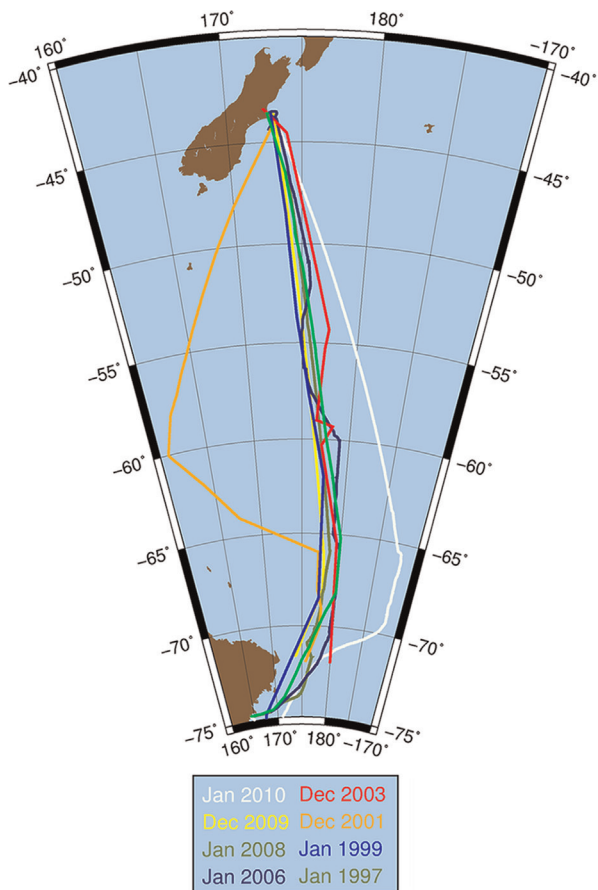


Fig. 2. Routes of the M/V *Italica* between New Zealand and Antarctica along which flask air samples were collected during eight cruises between 1997 and 2010. Atmospheric CO<sub>2</sub> concentrations were measured during 1998–1999, 2003–2004, 2005–2006, 2009 and 2010 cruises.

2001, 2005, 2007) was used to record CO<sub>2</sub> concentrations in the ocean atmosphere. The measurement system was based on the comparison between signals from two infrared absorbing cells, one filled with a flux of synthetic air with a constant CO<sub>2</sub> concentration and the other filled with the air sample. The air was carefully dried by means of a cold trap ( $t < -50^\circ\text{C}$ ). The instrument was calibrated using the WMO-X85 scale by means of various working standards with concentrations of 345, 375, 378 and 435 ppmv carefully determined at the Monte Cimone Observatory (Sestola, Italy), a baseline site of the Italian Meteorological Service. Air samples were collected in 4L Pyrex flasks, evacuated to better than  $5 \times 10^{-3}$  mmHg. They were opened on the windward side of the ship at about 15 m above sea level, closed with greaseless high vacuum stop-cocks and then stored in wooden boxes until the ship's return to Italy, 3–4 months later. Treatment of air samples for quantitative separation of CO<sub>2</sub> was carried out in the

laboratory. As reported in previous papers (Longinelli et al., 2007, 2010), the air samples from the flasks were pumped in a high vacuum line, at a rate of about 8–9 mL min<sup>-1</sup>, through a Swagelok microvalve and a liquid nitrogen-cooled spiral trap. When a final pressure lower than  $5 \times 10^{-3}$  mmHg was reached, the trap was heated at about  $-80^\circ\text{C}$  by means of an ethyl alcohol/liquid nitrogen slush and the evolved CO<sub>2</sub> was transferred in a sample tube and measured in a Finnigan Delta S mass spectrometer.

The isotopic values are reported in terms of delta units. Delta ( $\delta$ ) is defined by the relationship:  $\delta = [R_{\text{sample}} / R_{\text{stand.}} - 1] \times 10^3$ , where  $R = {}^{13}\text{C}/{}^{12}\text{C}$  or  ${}^{18}\text{O}/{}^{16}\text{O}$ .

Measurements were carried out against a standard CO<sub>2</sub> obtained from a very pure Carrara marble, the isotopic composition of which is  $-2.43\text{‰}$  ( $\delta^{18}\text{O}$  vs. VPDB) and  $+2.45\text{‰}$  ( $\delta^{13}\text{C}$  vs. VPDB), calibrated periodically versus NBS-19 and NBS-20. The values used for this calibration are: NBS-19,  $-2.20\text{‰}$  ( $\delta^{18}\text{O}$ ) and  $+1.95\text{‰}$  ( $\delta^{13}\text{C}$ ); NBS-20,  $-4.14\text{‰}$  ( $\delta^{18}\text{O}$ ) and  $-1.06\text{‰}$  ( $\delta^{13}\text{C}$ ).<sup>1</sup>

All carbon isotope data are reported versus the VPDB standard. The accuracy of our procedure was tested, before running each set of flasks, on several flask air samples collected simultaneously outside the laboratory and treated with the same technique. The standard deviation of the carbon isotope values obtained from these samples in different years ranged from  $\pm 0.02\text{‰}$  to  $\pm 0.04\text{‰}$  ( $1\sigma$ ). We believe that the reproducibility of the samples collected over the ocean is not far from these values. Although we are perfectly aware that this reproducibility is quite poor when compared, for instance, with that obtained by NOAA on land-based samples, lack of funding for this research prevented us from obtaining more accurate (and more expensive) extraction lines.

Carbon isotope results obtained from mass spectrometer analyses were corrected for the N<sub>2</sub>O effect according to the Mook and Van der Hoek (1983) equation:

$$\delta^{13}\text{C} - \delta^{13} = (343 \pm 6) \rho E \quad (1)$$

where  $\delta^{13}\text{C}$  is the true isotopic value of the CO<sub>2</sub> sample,  $\delta^{13}$  is the measured isotopic value, calculated as if N<sub>2</sub>O were absent,  $\rho$  is the N<sub>2</sub>O/CO<sub>2</sub> concentration ratio in the atmosphere and E is the ratio between the ionisation efficiencies for N<sub>2</sub>O and CO<sub>2</sub> in the mass spectrometer.

<sup>1</sup>NBS 20 standard material has not been available for a very long time. We had reasonable amounts of NBS 19 and NBS 20 inherited from various research centres where the senior author has worked in the past. All the NBS 20 has been consumed and we now face the serious problem of finding a reliable reference material to calibrate our laboratory standard. The existing LSVEC is isotopically too far from our Carrara laboratory standard, both in oxygen and carbon, and is consequently unreliable for calibration purposes.

N<sub>2</sub>O concentrations along the ship's route could not be directly measured, as the equipment on board the M/V *Italica*, was totally inadequate. Consequently, to correct  $\delta^{13}\text{C}$  measured on CO<sub>2</sub> from flask air samples, we calculated  $\rho$  using the mean value of N<sub>2</sub>O and CO<sub>2</sub> concentrations reported by NOAA for the Cape Green (Tasmania) and South Pole stations during the same periods of our sample collection. This is obviously an oversimplification, but it was the only way of evaluating an average correction of the measured  $\delta^{13}\text{C}$  values. According to NOAA data,  $\rho$  values at the time of the 2004/2005, 2005/2006 and 2009 and 2010 cruises varied between  $0.836 \times 10^{-3}$  and  $0.847 \times 10^{-3}$ .  $E$  was calculated as 0.6161 (as determined by Finnigan engineers on an instrument identical to our mass spectrometer). The value of the right member of eq. (1) may thus vary from 0.1735 to 0.1821, so that the possible overall error in the corrected  $\delta^{13}\text{C}$  value is, at most, in the hundredths of a unit. As the error of measurement is probably at least two times larger, to standardise the corrections, the mean value of 0.178 was used for all flask air samples (Tables 1–4). The correction value has not changed substantially during

the last few years (Longinelli et al., 2005) because of the simultaneous increase of both N<sub>2</sub>O and CO<sub>2</sub> concentrations and the use of the same mass spectrometer for isotopic measurements.

### 3. Results and discussion

The carbon isotope composition of CO<sub>2</sub> from flask air samples collected during the first four cruises from New Zealand to Antarctica (1998–1999, 2001–2002, 2002–2003 and 2003–2004) were reported graphically by Longinelli et al. (2007) (Fig. 1). Samples were always collected during the same period of the year, between late December and early January along similar routes (Fig. 2). The results show a rather large variability, an increasing frequency over time of isotopically light values and the lightest values concentrated in a latitudinal belt of about 15° across the Polar Front.

The 2004–2005 air samples yielded  $\delta^{13}\text{C}$  values which were totally different from those obtained from previous cruises. Twenty-four flask air samples were collected between 31 December 2004 and 6 January 2005, from

Table 1.  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> (New Zealand to Antarctica, 2004–2005)

Sample No.	UTC date	UTC hour	Latitude (S)	Longitude (E)	$\delta^{13}\text{C} \text{ ‰}$ (VPDB)	$\delta^{13}\text{C} \text{ ‰}^a$ (VPDB)	CO <sub>2</sub> ppmv
1	Dec. 31, 2004	09.39	44.00.31	173.19.30	−8.90	−8.72	374
2	Jan. 1, 2005	04.14	47.58.45	174.12.75	−9.19	−9.01	334
3	Jan. 1, 2005	09.20	49.02.30	174.29.59	−9.42	−9.24	351
4	Jan. 1, 2005	14.15	50.00.65	174.42.41	−8.94	−8.76	381
5	Jan. 1, 2005	19.35	51.02.33	174.56.50	−8.81	−8.63	382
6	Jan. 2, 2005	00.45	52.01.40	175.06.50	−9.00	−8.82	391
7	Jan. 2, 2005	05.50	52.58.61	175.01.16	−9.24	−9.06	363
8	Jan. 2, 2005	11.05	54.00.91	174.57.30	−8.96	−8.78	380
9	Jan. 2, 2005	16.58	54.58.03	174.50.19	−9.31	−9.13	362
10	Jan. 2, 2005	23.03	56.00.67	174.43.26	−9.08	−8.90	373
11	Jan. 3, 2005	04.29	57.01.55	174.38.31	−8.89	−8.71	393
12	Jan. 3, 2005	09.42	58.00.89	174.33.74	−9.29	−9.11	364
13	Jan. 3, 2005	14.56	59.00.19	174.26.53	−9.21	−9.03	368
14	Jan. 3, 2005	19.50	60.01.28	174.17.81	−8.85	−8.67	404
15	Jan. 4, 2005	00.25	61.01.05	174.33.10	−9.01	−8.83	378
16	Jan. 4, 2005	04.56	62.00.87	174.51.26	−9.40	−9.22	357
17	Jan. 4, 2005	21.20	63.02.60	175.08.13	−8.96	−8.78	380
18	Jan. 5, 2005	02.07	64.05.02	175.36.50	−9.44	−9.26	353
19	Jan. 5, 2005	06.08	65.00.34	175.48.15	−8.83	−8.65	381
20	Jan. 5, 2005	10.50	66.00.12	176.27.07	−9.19	−9.01	358
21	Jan. 5, 2005	16.00	66.59.91	177.32.16	−8.83	−8.65	399
22	Jan. 5, 2005	23.20	67.59.81	178.23.26	−9.24	−9.06	367
23	Jan. 6, 2005	07.55	68.57.58	178.02.44	−9.07	−8.89	375
24	Jan. 6, 2005	20.21	70.54.05	175.00.60	−9.05	−8.87	378

<sup>a</sup>After correction for the N<sub>2</sub>O effect.

<sup>b</sup>These values are only rough evaluations of the CO<sub>2</sub> concentrations calculated from the CO<sub>2</sub> pressure of each sample in the source of the mass spectrometer.

Table 2.  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> (New Zealand to Antarctica, 2006)

Sample No.	UTC date	UTC hour	Latitude (S)	Longitude (E)	$\delta^{13}\text{C}$ ‰ (VPDB)	$\delta^{13}\text{C}$ ‰ <sup>a</sup> (VPDB)	CO <sub>2</sub> ppmv
25	Jan. 1	02.58	47.58.20	174.35.00	−8.65	−8.48	377.1
26	Jan. 1	08.07	49.02.00	174.56.00	−8.72	−8.55	377.8
27	Jan. 1	12.11	49.56.00	175.13.08	−9.20	−9.03	378.0
28	Jan. 1	20.14	51.04.00	175.37.00	−9.78	−9.60	379.7
29	Jan. 2	0.33	52.00.87	175.44.21	−10.02	−9.84	380.5
30	Jan. 2	05.07	53.02.52	175.25.17	−10.02	−9.84	not avail.
31	Jan. 2	09.34	54.59.45	175.03.87	−11.22	−11.04	377.0
32	Jan. 2	14.19	54.59.19	174.49.35	−9.04	−8.86	not avail.
33	Jan. 2	19.53	56.05.70	174.59.84	−10.26	−10.08	not avail.
34	Jan. 3	01.08	57.00.07	175.34.90	−9.19	−9.01	377.3
35	Jan. 3	07.04	58.01.73	176.28.52	−9.60	−9.42	377.3
36	Jan. 3	12.48	58.59.59	177.32.44	−9.04	−8.86	377.4
37	Jan. 3	21.59	60.01.00	179.00.61	−13.63	−13.45	376.9
38	Jan. 4	05.12	61.02.00	179.00.11	−9.33	−9.15	376.8
39	Jan. 4	10.24	62.00.00	178.59.51	−9.00	−8.82	377.1
40	Jan. 4	19.17	63.03.00	178.59.51	−8.93	−8.75	376.8
41	Jan. 4	23.19	64.00.85	179.05.22	−8.78	−8.60	376.8
42	Jan. 5	04.58	65.00.69	179.00.77	−9.99	−9.81	376.5
43	Jan. 5	12.02	66.00.44	179.47.27 W	−8.95	−8.77	377.1
44	Jan. 5	20.19	67.26.00	179.08.00	−10.61	−10.43	377.3
45	Jan. 6	01.54	68.03.11	179.54.84	−9.11	−8.93	377.3

<sup>a</sup>After correction for the N<sub>2</sub>O effect.

about 44° S to about 71° S. The numerical results are listed in Table 1 and shown in Fig. 3a. Their saw-toothed distribution is clearly inexplicable and almost unbelievable. Systematic errors of measurement, although highly improbable, could hardly have produced the saw-toothed distribution of Fig. 3a for which we can find no acceptable explanation. During this cruise, no direct measurements of atmospheric CO<sub>2</sub> concentrations could be carried out. To have at least a rough idea of the CO<sub>2</sub> concentrations in each sample, we tried to calculate the amount of CO<sub>2</sub> from

the gas pressure of each sample in the mass spectrometer source, after calibration with known CO<sub>2</sub> volumes. The method is obviously not quantitative, and the results obtained were quite surprising. Not only did the CO<sub>2</sub> concentrations repeat the saw-toothed distribution of the  $\delta^{13}\text{C}$  values but also, strangely enough, higher CO<sub>2</sub> concentrations corresponded to heavier  $\delta^{13}\text{C}$  values and vice-versa. The measured  $\delta^{13}\text{C}$  values and calculated CO<sub>2</sub> concentrations are shown graphically in Fig. 3b. We believe that this self-contradictory distribution of values can

Table 3.  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> (New Zealand to Antarctica, 2009)

Sample No.	UTC date	UTC hour	Latitude S	Longitude	Flask	$\delta^{13}\text{C}$ ‰ (VPDB)	$\delta^{13}\text{C}$ ‰ <sup>a</sup> (VPDB)	CO <sub>2</sub> ppmv
1	Dec. 20	2:42	50.17.82	176.47.66 E	Ff	−9.05	−8.87	383.0
2	Dec. 20	19:15	53.20.27	178.49.30 E	Fg	−8.90	−8.72	383.3
3	Dec. 21	8:17	56.04.75	179.37.96 W	Fh	−8.87	−8.69	383.3
4	Dec. 21	20:00	58.46.00	177.45.10 W	Fi	−8.88	−8.70	383.0
5	Dec. 22	3:00	60.21.26	176.36.68 W	Fl	−8.85	−8.67	382.5
6	Dec. 22	10:51	62.13.01	175.09.52 W	Fa	−8.88	−8.70	382.7
7	Dec. 22	20:30	64.20.52	173.24.05 W	Fb	−8.88	−8.70	382.7
8	Dec. 23	9:47	66.43.25	171.51.59 W	Fc	−8.80	−8.62	382.5
9	Dec. 23	22:50	68.37.52	172.05.34 W	Fd	−8.79	−8.61	Not available
10	Dec. 24	12:45	70.08.05	173.34.82 W	Fe	−8.81	−8.63	382.4

<sup>a</sup>After correction for the N<sub>2</sub>O effect.



Table 4.  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  (New Zealand to Antarctica, 2010)

Sample No.	UTC date	UTC hour	Latitude S	Longitude E	Flask	$\delta^{13}\text{C} \text{ ‰}$ (VPDB)	$\delta^{13}\text{C} \text{ ‰}^a$ (VPDB)	$\text{CO}_2$ ppmv
1	Jan. 25	2:55	45.03.30	173.24.91	Da	−8.88	−8.70	383.5
2	Jan. 25	10:52	46.59.09	173.44.28	Db	−8.91	−8.73	383.4
3	Jan. 25	19:32	49.00.93	174.05.69	Dc	−8.52	−8.34	383.0
4	Jan. 26	4:08	51.00.13	174.27.06	Dd	−8.84	−8.66	383.1
5	Jan. 26	10:27	52.28.19	174.43.58	De	−8.56	−8.38	382.3
6	Jan. 26	19:56	54.36.89	175.08.65	Df	−8.56	−8.38	383.5
7	Jan. 27	0:18	55.36.94	175.20.72	Dg	−8.54	−8.36	383.4
8	Jan. 27	3:54	56.29.59	175.31.99	Dh	−8.60	−8.42	384.0
9	Jan. 27	7:25	57.19.90	175.42.96	Ca	−8.79	−8.61	384.3
10	Jan. 27	10:22	58.02.24	175.02.24	Cb	−8.60	−8.42	384.7
11	Jan. 27	18:26	60.00.09	176.18.89	Cc	−8.67	−8.49	383.1
12	Jan. 27	22:42	61.00.07	176.32.75	Cd	−8.58	−8.40	383.9
13	Jan. 28	3:11	62.00.37	174.47.77	Ce	−8.55	−8.37	383.1
14	Jan. 28	7:33	63.00.11	177.02.62	Cf	−8.55	−8.37	382.8
15	Jan. 28	10:57	63.46.82	177.14.88	Cg	−8.57	−8.39	382.4
16	Jan. 28	19:04	65.41.43	177.46.65	Ch	−8.58	−8.40	382.5
17	Jan. 28	22:36	66.31.99	177.59.74	Ba	−8.54	−8.36	382.5
18	Jan. 28	2:41	67.32.17	178.00.31	Bb	−8.56	−8.38	382.9
19	Jan. 29	7:02	68.33.27	177.25.74	Bc	−8.59	−8.41	Not available
20	Jan. 29	11:08	69.28.50	176.27.27	Bd	−8.55	−8.37	382.6

<sup>a</sup>After correction for the  $\text{N}_2\text{O}$  effect.

hardly result from errors in measuring the two variables; however, we are unable to find a reliable interpretation for these puzzling data.

During the 2005–2006 cruise, 21 flask air samples were collected between 1 January 2006 and 6 January 2006: two of them south of New Zealand's South Island and 19 between 49.56.00 S and 68.03.11 S. The  $\delta^{13}\text{C}$  measurements of  $\text{CO}_2$  from the flask air samples are listed in Table 2 and shown in Fig. 4. The two results from the samples collected not far from the southern coast of New Zealand are close to  $-8.5 \text{ ‰}$  whereas almost all the others are more negative, four of them showing the lightest values ever measured between New Zealand and Antarctica. Sample 31, from 54.59.45 S, has a  $\delta^{13}\text{C}$  value of  $-11.04 \text{ ‰}$ ; sample 33, from 56.05.70 S, has a  $\delta^{13}\text{C}$  of  $-10.08 \text{ ‰}$ ; sample 37, from 60.01.00 S, shows  $-13.45 \text{ ‰}$  and sample 44, from 67.26.00 S, has  $-10.43 \text{ ‰}$ . After the interval of the inexplicable results of the 2004–2005 cruise, these data seem to represent an evolution of the situation found during the previous 2002–2003 and 2003–2004 cruises, with more frequent and more negative isotopic events recorded. With the only exception of sample 29 (higher  $\text{CO}_2$  concentration and more negative  $\delta^{13}\text{C}$ ), no major changes in  $\text{CO}_2$  concentrations were detected as quantitatively related to the measured changes in the  $\delta^{13}\text{C}$  values. This may be due to the instrumental method of measurement, since the Siemens Ultramat 5E analyser integrates the values measured every 2 seconds every 10 minutes, so that large transient changes

may be practically obliterated by the integration process. The hypothesis of contamination from the ship's exhaust had already been discussed by Longinelli et al. (2007) and ruled out for several reasons. Consequently, these results may be essentially related to small-scale, positive air–sea fluxes with various causes, such as upwelling of deep waters with elevated concentrations of dissolved inorganic carbon, the possible contribution of biological heterotrophic activity, production of isotopically light  $\text{CO}_2$  by remineralization of decomposing Particulate Organic Matter (POM), and so on. As already reported in the introduction, many authors agree about the possibility of outgassing events of  $\text{CO}_2$  from sea-water to the atmosphere in the circumpolar areas; the statement by Zickfeld et al. (2008) on the possible contribution to the atmosphere of  $\text{CO}_2$  from upwelling deep waters being particularly interesting.

However, some of the 2005–2006 results are puzzling, such as the rather negative values obtained while the ship was sailing near the edge of the Campbell Plateau, at latitudes between about  $50^\circ$  and  $52^\circ$  S (samples 27, 28 and 29: Table 2 and Fig. 4), where the ocean depth is between 500 and 1000 m.

The  $\delta^{13}\text{C}$  results obtained from 1998 to 2006, shown in Fig. 5, seem to reinforce the hypotheses already suggested by Longinelli et al. (2007), with the only exception of the anomalous 2004–2005 data. After 2006, we were unable to obtain berths on the M/V *Italica* for 3 yr, and collection of discrete air samples and measurement of  $\text{CO}_2$

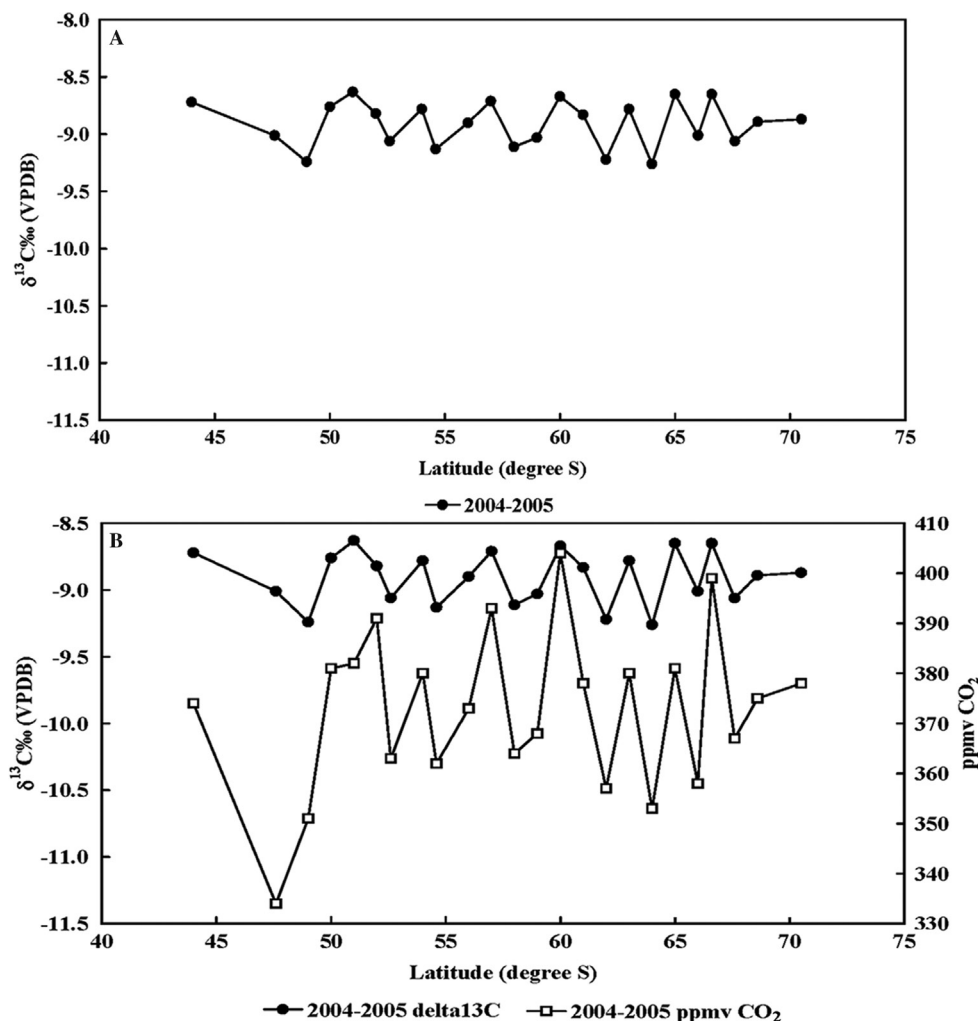


Fig. 3. (a)  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> from flask air samples collected between New Zealand and Antarctica during 2004–2005 cruise. CO<sub>2</sub> concentrations could not be measured during this cruise. (b)  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> from flask air samples (2004–2005 cruise). CO<sub>2</sub> concentrations in each sample were roughly evaluated from CO<sub>2</sub> gas pressure of each sample in the mass spectrometer source, after calibration with known CO<sub>2</sub> volumes.

concentrations between New Zealand and Antarctica were compulsorily discontinued. We lack information which might have shown some connection between the results of 2006 and those of 2009, when we were again able to develop our work on board the *Italica* and repeat air sample collections twice (20–24 December 2009 and 25–29 January 2010), taking advantage of a double crossing from New Zealand to Antarctica. During the former voyage, 10 flask air samples were collected from 50.18.82 S to 70.08.05 S, and 20 samples during the latter one, from 45.03.30 S to 69.28.50 S. CO<sub>2</sub> concentrations were recorded during both cruises, so that we can now compare the two variables along the ship's course. These flask air samples were treated according to the usual procedure, and the results are shown in Tables 3 and 4, respectively. To our surprise,

the air samples collected during these two cruises showed extremely homogeneous carbon isotopic compositions:  $-8.69 \pm 0.07$  ‰ for the 10 samples in 2009 and  $-8.44 \pm 0.12$  ‰ for the 20 samples in 2010. The mean value of the 2010 samples was close to the background values of recent years which ranged from about  $-8.0$  to about  $-8.3$  in the decade 2002–2012 (values measured at the NOAA stations of Mahé Island, Indian Ocean, Cape Grim, Tasmania, Crozet Island, Southern Indian Ocean and the Japanese Syowa station, the Antarctica coast, from the beginning to the end of that decade).

The isotopic results are shown in Figs. 6 and 7, and in this case the homogeneity of the results is even more striking, in sharp contrast with both the variability of isotopic results found during previous cruises and the

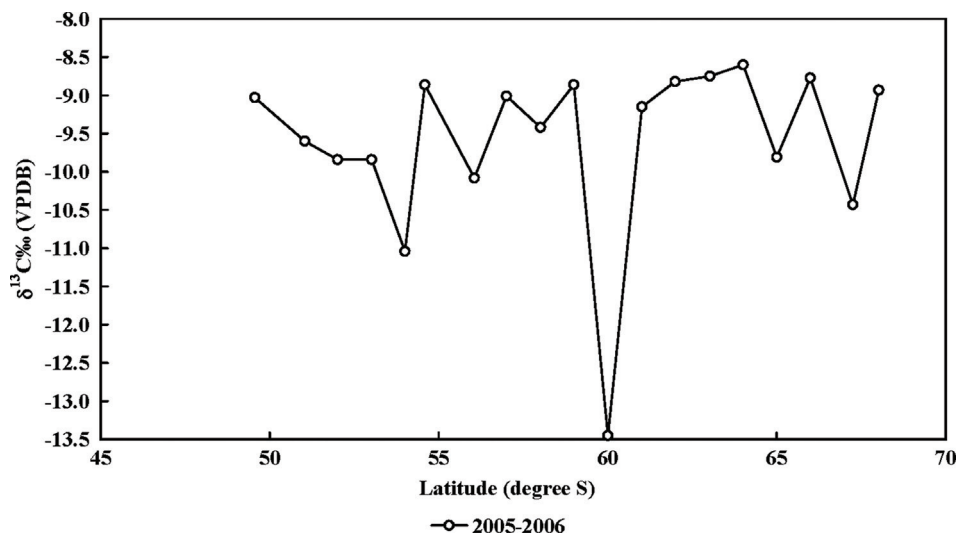


Fig. 4.  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  from flask air samples collected between New Zealand and Antarctica during 2005–2006 cruise.

expected tendency to a progressive increase in negative events and an evolution of isotopic values towards  $^{13}\text{C}$ -depleted values. In both cases, the  $\text{CO}_2$  concentrations show very homogeneous and very low values. When we calculate their mean value measured in 2006 (377.5 ppmv) and that for the 2010 cruise (383.2 ppmv), the calculated growth rate is  $1.4 \text{ ppmv y}^{-1}$ . This is lower than the values calculated at the two closest land-based stations: the NOAA Cape Grim station (Tasmania) close to  $1.7 \text{ ppmv y}^{-1}$  and the Japanese Syowa station (North Antarctic coast), also close to  $1.7 \text{ ppmv y}^{-1}$ .

The  $\delta^{13}\text{C}$  from the air samples collected over five expeditions (Fig. 5) reasonably match the conclusions of Takahashi et al. (2009), who located a large ‘positive’ area

between New Zealand and Antarctica (between about  $55^\circ$  and  $70^\circ \text{ S}$ ) which is to be considered a probable source of  $\text{CO}_2$ . As already suggested by Longinelli et al. (2007), the contribution to the atmosphere of isotopically light  $\text{CO}_2$  may have several causes. Upwelling of deep waters particularly rich in isotopically light-dissolved  $\text{CO}_2$  normally occurs at relatively high latitudes, but the upwelled water may then be transported north by Ekman transport and, after mixing with Antarctic Surface Water, partially liberate its  $\text{CO}_2$  to the atmosphere, thus modifying the background  $\delta^{13}\text{C}$ , particularly in the lower layers of the atmosphere where our flask samples were collected. The carbon isotope composition of the  $\text{CO}_2$  dissolved in deep waters is largely derived by remineralization of POM and may be extremely

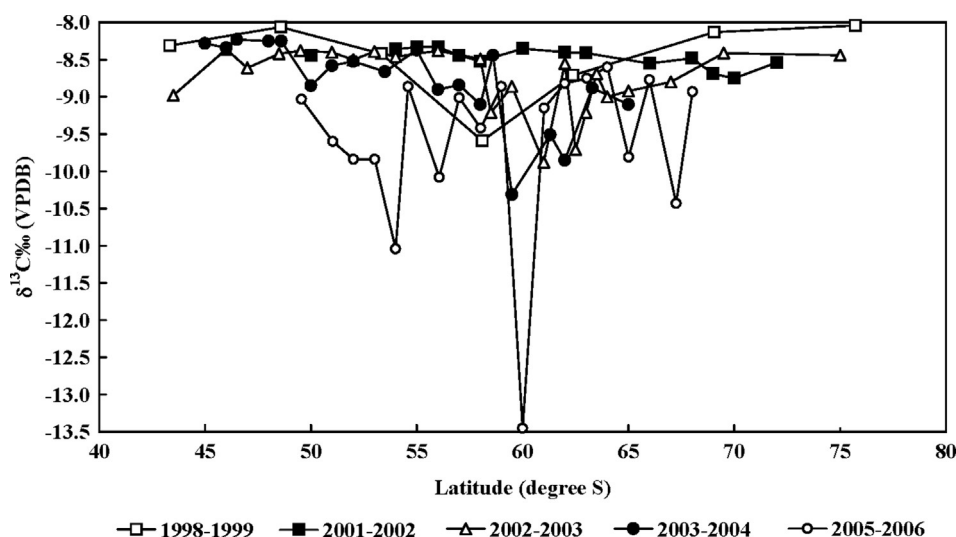


Fig. 5.  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  from flask air samples collected between New Zealand and Antarctica during five cruises between 1998–1999 and 2005–2006.



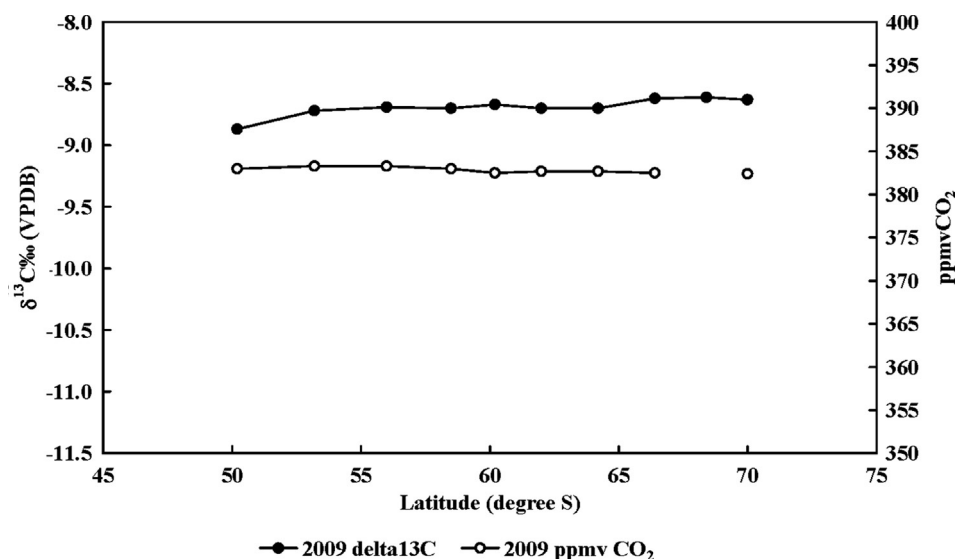


Fig. 6.  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> from flask air samples and CO<sub>2</sub> concentrations measured between New Zealand and Antarctica in December 2009.

negative, the  $\delta^{13}\text{C}$  of marine POM reaching values as low as  $-16$  to  $-35$  ‰ (VPDB) (Fontugne and Duplessy, 1981; Fontugne et al., 1991; François et al., 1993; Goericke and Fry, 1994; Kennedy and Robertson, 1995; Bentaleb et al., 1998; Lourey et al., 2004).

Near-surface turbulence and wave breaking may enhance outgassing. The possibility of a CO<sub>2</sub> increase in the surface layer due to the influx of CO<sub>2</sub> related to eddy-diffusive influx from underlying water layers was already discussed by Stoll et al. (2002). At high latitudes, the recorded number of negative isotopic events tends to

decrease and CO<sub>2</sub> isotopic values tend to increase, while surface waters at high latitudes are generally characterised by high concentrations of CO<sub>2</sub> with low  $\delta^{13}\text{C}$  values because of the contribution of upwelling water masses. The decrease in isotopically light events may be due to surface water temperatures which, south of the Polar Front, are generally close to or even below zero (Craig et al., 1981; Rintoul et al., 1997; Russo et al., 1999). These temperature conditions may prevent, or at least drastically reduce, positive air–sea fluxes because of the increasing solubility of CO<sub>2</sub> at low temperatures.

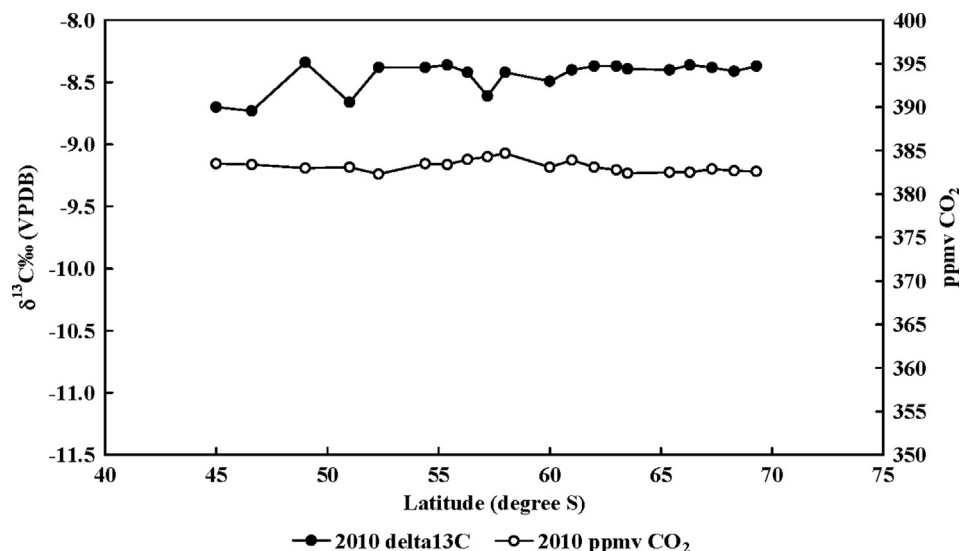


Fig. 7.  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> from flask air samples and CO<sub>2</sub> concentrations measured between New Zealand and Antarctica in January 2010.

As previously mentioned, the results from the 2004 to 2005 cruise (Table 1, Fig. 3) do not allow any reasonable interpretation, whereas the 2009 and 2010 results indicate environmental conditions which exclude any positive contribution of CO<sub>2</sub> to the atmosphere from the sea surface. During these two last cruises, technical problems prevented the recording of wind speed and direction. However, in the unanimous opinion of the ship's crew, these cruises, particularly that of 2010, were particularly quiet, with almost calm seas and low wind, environmental conditions which may have contributed to the results obtained.

The lack of sampling from 2006 to 2009 does not help us to understand whether the results obtained during 2009 and 2010 cruises are due to substantial annulment of the processes which caused the negative episodes recorded in previous years or due to fortuitous conditions of the ocean and atmospheric dynamics. As already noted, the impossibility of using an oceanographic ship for these cruises prevented us from collecting data on many other variables, such as vertical profiles of seawater temperature, seawater–atmosphere temperature gradients, concentration of dissolved CO<sub>2</sub> in surface water, biological autotrophic versus heterotrophic activity in surface waters, and so on, which may have been of importance to relate the results to definite environmental conditions.

#### 4. Summary and conclusions

Discrete air samples collected during eight cruises between New Zealand and Antarctica during austral summers between 1998 and 2010 revealed a large variety of  $\delta^{13}\text{C}$  values of atmospheric CO<sub>2</sub>. Samples from five cruises (1998–1999, 2001–2002, 2002–2003, 2003–2004 and 2005–2006) showed increasing episodes of isotopically light CO<sub>2</sub> in the lower atmosphere,  $\delta^{13}\text{C}$  values ranging from slightly lighter than background values (–8.0 to about –8.4 ‰) down to –13.45 ‰. The lack of direct measurements of several variables of environmental conditions prevented us from suggesting precise causes for these episodes. Isotopic results from the 2004 to 2005 cruise are a sort of improbable puzzle; they could hardly have been caused by systematic errors of measurement but are definitely beyond any reasonable interpretation. The data from the last two sets of samples (December 2009 and January 2010) greatly differ from the results from previous cruises, showing absolutely flat  $\delta^{13}\text{C}$  values, paralleled by flat CO<sub>2</sub> concentrations. We hope that further air sampling in the same area (samples have been collected in January 2012) will show whether they should be viewed as constituting only a fortuitous episode or as the beginning of a substantially different trend possibly caused by changes in the oceanic circulation related to changes in the climatic conditions.

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