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CO_2 maximum in the oxygen minimum zone (OMZ)

A. Paulmier[1], **D. Ruiz-Pino**[2], **and V. Garçon**[1]

[1]LEGOS, IRD/CNRS, UMR 5566, 18 av. Ed Belin, 31401 Toulouse Cedex 9, France
[2]LOCEAN, UMR 7159, Université Pierre et Marie Curie, Courrier 134, 4 pl. Jussieu, 75 252 Paris Cedex 05, France

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Abstract. Oxygen minimum zones (OMZs), known as suboxic layers which are mainly localized in the Eastern Boundary Upwelling Systems, have been expanding since the 20th "high CO_2" century, probably due to global warming. OMZs are also known to significantly contribute to the oceanic production of N_2O, a greenhouse gas (GHG) more efficient than CO_2. However, the contribution of the OMZs on the oceanic sources and sinks budget of CO_2, the main GHG, still remains to be established.

We present here the dissolved inorganic carbon (DIC) structure, associated locally with the Chilean OMZ and globally with the main most intense OMZs ($O_2 < 20\,\mu mol\,kg^{-1}$) in the open ocean. To achieve this, we examine simultaneous DIC and O_2 data collected off Chile during 4 cruises (2000–2002) and a monthly monitoring (2000–2001) in one of the shallowest OMZs, along with international DIC and O_2 databases and climatology for other OMZs.

High DIC concentrations ($>2225\,\mu mol\,kg^{-1}$, up to $2350\,\mu mol\,kg^{-1}$) have been reported over the whole OMZ thickness, allowing the definition for all studied OMZs a Carbon Maximum Zone (CMZ). Locally off Chile, the shallow cores of the OMZ and CMZ are spatially and temporally collocated at 21° S, 30° S and 36° S despite different cross-shore, long-shore and seasonal configurations. Globally, the mean state of the main OMZs also corresponds to the largest carbon reserves of the ocean in subsurface waters. The CMZs-OMZs could then induce a positive feedback for the atmosphere during upwelling activity, as potential direct local sources of CO_2. The CMZ paradoxically presents a slight "carbon deficit" in its core (∼10%), meaning a DIC increase from the oxygenated ocean to the OMZ lower than the corresponding O_2 decrease (assuming classical C/O molar ratios). This "carbon deficit" would be related to regional thermal mechanisms affecting faster O_2 than DIC (due to the carbonate buffer effect) and occurring upstream in warm waters (e.g., in the Equatorial Divergence), where the CMZ-OMZ core originates. The "carbon deficit" in the CMZ core would be mainly compensated locally at the oxycline, by a "carbon excess" induced by a specific remineralization. Indeed, a possible co-existence of bacterial heterotrophic and autotrophic processes usually occurring at different depths could stimulate an intense aerobic-anaerobic remineralization, inducing the deviation of C/O molar ratios from the canonical Redfield ratios. Further studies to confirm these results for all OMZs are required to understand the OMZ effects on both climatic feedback mechanisms and marine ecosystem perturbations.

1 Introduction

The most intense ($O_2 < 20\,\mu mol\,kg^{-1}$) and largest oxygen minimum zones (OMZs), known as suboxic layers, are mainly localized in subsurface of the upwelling regions in the Eastern Pacific and Northern Indian open oceans (Paulmier and Ruiz-Pino, 2008). OMZs can be considered as analogs of the primitive anoxic ocean associated with a high CO_2 atmosphere (>1000 ppmv: Royer et al., 2004), because of comparable reduced chemical conditions and similarities between ancient bacteria and those living in the OMZs (e.g., Planctomycetales: Gribaldo and Philippe, 2002). OMZs appear as a refuge of abundant specific microbes capable of chemolithoautrophic carbon assimilation (Walsh et al., 2009) and organisms adapted to low O_2 (e.g., zooplankton as specific copepods and euphausiids: Wishner et al., 2008; Antezana, 2009). These biological specificities and perturbations, associated with shifts in animal distribution and changes in ecosystems structure (e.g., towards gelatinous species as jellyfish and salps: Childress and Siebel, 1998), may potentially impact the carbon export. In addition, OMZs

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Correspondence to: A. Paulmier
(aurelien.paulmier@legos.obs-mip.fr)

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are submitted to climate change (lower ventilation by stratification and O_2 solubility decrease) and natural or anthropogenic fertilization (remineralization increase) through nutrient or metal inputs by upwelling, rivers or dust (Fuhrman and Capone, 1991; Naqvi et al., 2006; Rabalais et al., 2010). In the past, OMZs have probably extended and contracted in warm (interglacial) and cold (glacial) periods (e.g., Cannariato and Kennett, 1999; Rogers, 2000), associated with high (300 ppmv) and low (180 ppmv) atmospheric CO_2 (Jansen et al., 2007), respectively. In the present and according to the last decades observations associated with high anthropogenic CO_2 uptake by the ocean (Sabine et al., 2004), OMZs would increase or intensify (Stramma et al., 2008), or even new ones appear locally and episodically (Chan et al., 2008).

OMZs are known for playing an essential role in the nitrogen cycle, in which different autotrophic and heterotrophic bacterial processes intervene (e.g., Arrigo, 2005) such as ammonification, nitrogen assimilation, anammox, DNRA (dissimilatory nitrate reduction to ammonia), denitrification and nitrification. As a result of these two last processes, OMZs would produce up to 50% of the oceanic N_2O (e.g., Bange, 2008), a greenhouse gas, ~300 times more efficient than CO_2 (Jain et al., 2000; Ramaswamy et al., 2001). So far, no study has investigated the direct link between OMZs and the most important greenhouse gas, CO_2.

However, OMZs may play an indirect role on the carbon reservoir through denitrification which converts nitrate, one of the main oceanic nutrients, into gaseous nitrogen (e.g., N_2, N_2O) lost towards the atmosphere. Indeed, according to Falkowski's (1997) hypothesis, the denitrification process would decrease the oceanic nitrogen reserve and consequently the total primary production reduction will limit atmospheric CO_2 sequestration by the ocean. In addition, Koeve and Kähler (2010) show theoretically that the combined effects of the processes in the OMZ core turn out to be clearly heterotrophic, suggesting net direct OMZ CO_2 release.

The main objective of this study is, therefore, to determine and discuss the total CO_2 or DIC (dissolved inorganic carbon) structures which are forming in the OMZs, from a local and temporal study focused in the OMZ off Chile and extended to the global ocean.

Indeed, the eastern tropical south Pacific (ETSP) OMZ is well suited for a detailed study. The ETSP presents high DIC concentrations in subsurface ($>2250\ \mu\text{mol kg}^{-1}$; e.g., Copin-Montégut and Raimbault, 1995), mainly reported in very local areas. Because the ETSP presents the shallowest OMZ (Paulmier and Ruiz-Pino, 2008), the ETSP OMZ is closely exposed to ocean-atmosphere CO_2 exchanges, which may be amplified by the intense upwelling activity (Strub et al., 1998). Its almost double (new and export) primary production ($855\ \text{gC m}^{-2}\ \text{yr}^{-1}$: Chavez and Messié, 2009) associated with less intense anthropogenic influence (Doney et al., 2007) as compared with the eastern tropical north Pacific (ETNP) allows to study the DIC structure naturally associated with the OMZ.

In particular, the OMZ off Chile (cf. Paulmier et al., 2006) is characterised by a shallow (5–20 m) very intense ($>1\ \mu\text{mol kg}^{-1}\ \text{m}^{-1}$) and stratified oxycline associated with an O_2 continuum from oxic ($O_2 > 200\ \mu\text{mol kg}^{-1}$) to suboxic ($O_2 < 20\ \mu\text{mol kg}^{-1}$) and intercepting the euphotic layer depth. The Chilean OMZ also presents a very low oxygenated core ($O_2 < 20\ \mu\text{mol kg}^{-1}$, down to $<1\ \mu\text{mol kg}^{-1}$), which is one of the thickest relative to the upper and lower O_2 gradients (Paulmier and Ruiz-Pino, 2008), allowing a significant denitrification (anerobic remineralization) activity (e.g., Graco, 2002). High DIC concentrations have been measured off Chile (e.g., Takahashi and Goddard, 1998; Torres, 2001), although never related with the OMZ influence. At the surface, separated studies indicate intense sources of CO_2 (at 23°–30° S: $\sim$+5 $\text{mmol m}^{-2}\ \text{d}^{-1}$; Torres, 2001; Lefèvre et al., 2002), 5 times higher than the oceanic average. In addition, locally in the OMZ off Chile, Paulmier et al. (2006) suggested a specific remineralization at the oxycline up to 5 times more intense than in the oxygenated ocean, which consequently produces more CO_2 than classically. However, and in addition to its specificity of being shallow and intercepting the euphotic layer, the OMZ off Chile is characterised by an important temporal variability. The primary production ($0.5\text{–}20\ \text{mgC m}^{-2}\ \text{d}^{-1}$: Daneri et al., 2000) and the sea surface biomass ($0.2\text{–}1.2\ \text{mg m}^{-3}$: Paulmier et al., 2006) are up to 3 times higher in summer and at the coast and in the centre (30–36° S) than in spring and winter, offshore and in the north (21° S), respectively. The air-sea CO_2 fluxes also present a high spatiotemporal modulation (between -3 and $25\ \text{mmol m}^{-2}\ \text{d}^{-1}$; Paulmier et al., 2008). Indeed, they can shift in austral summer and winter from an intense CO_2 source (e.g., $p\text{CO}_2 > 1000\ \mu\text{atm}$ at 23° S, Torres, 2001) to a strong sink (e.g., $p\text{CO}_2 < 150\ \mu\text{atm}$ at 30° S, Lefèvre et al., 2002). Thus, this work presents a DIC and O_2 dataset collected off Chile in order to study locally in detail the same 4 cruises (Fig. 1) and monitoring the specific DIC structure associated with an OMZ already described in Paulmier et al. (2006).

2 Methodology

To characterise locally the DIC structure associated with an OMZ, a high vertical resolution sampling (5–10 m), adapted to low O_2 concentrations ($<20\ \mu\text{mol kg}^{-1}$), has been performed simultaneously for DIC and O_2 in the OMZ off Chile to capture the intense biogeochemical gradients. This sampling is based on 3 sites (in the North: Iquique, 21° S; in the Centre: Coquimbo, 30° S; on the continental shelf, Concepción, 36° S) between 2000 and 2002 in non El Niño years during four cruises and a monthly monitoring. The four cruises have been performed at 21° S with a bottom depth of 80–1880 m (09/2000, day/night station; 05/2001, cross-shore

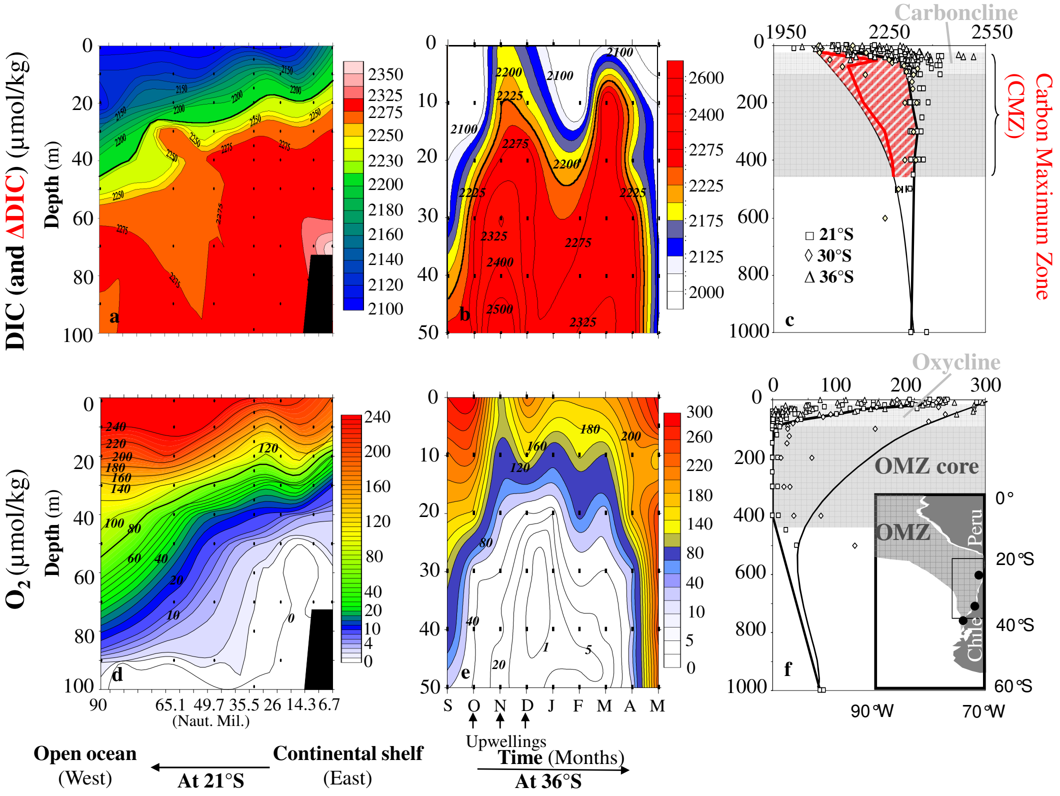

Fig. 1. Vertical sections along an east-west cross-shore transect on 0–100 m (DIC: **(a)**; O$_2$: **(d)** and versus time on 0–50 m (DIC: **(b)**; O$_2$: **(e)**. Points indicate sampling locations. Profiles of DIC **(c)** and O$_2$ **(f)** on 0–1000 m for all stations sampled in the OMZ off Chile in 2000–2002. Continuous thin profiles correspond to classical profiles out of the OMZ in the Eastern Equatorial Pacific (for DIC on **(c)**: Viecelli, 1984; for O$_2$ on **(f)**: Ivanoff, 1972). Continuous thick black profiles indicate representative profiles for DIC on **(c)** and for O$_2$ on **(f)**. On **c** and **f**, data from Iquique at 21° S (squares), Coquimbo at 30° S (diamonds) and Concepción at 36° S (triangles). On **(c)**: the hatched red area indicates DIC$_{\text{CMZ}}$ (DIC$_{\text{CMZ}}$ = DIC$_{\text{Average on OMZ}}$ − DIC$_{\text{Classical out of OMZ}}$) corresponding to the carbon maximum zone (CMZ); continuous thick red profile indicates the representative profile for the sum of DIC$_{\text{Classical out of OMZ}}$ and local DIC production contributing to the CMZ (DIC$_{\text{Classical out of OMZ}}$ + ΔDIC), with ΔDIC the biogeochemical contribution to DIC. The points on the map in **(f)** indicate the three sampled latitudes (21° S; 30° S; 36° S).

transect; 04/2002, biogeochemical station) and at 30° S with a bottom depth of 700–4000 m (04/2002, biogeochemical station). The monthly monitoring took place at 36° S off a semi-enclosed bay with a bottom depth of 60 m (from September 2000 to May 2001, S14 station). This sampling allows for the documentation of illustrative spatiotemporal variations, associated with different biogeochemical and dynamical regimes mentionned in the Introduction and detailed in Paulmier et al. (2006).

Total dissolved inorganic CO$_2$ (DIC) samples were analysed by potentiometry (Bradshaw and Brewer, 1988) with the National CO$_2$ measurement Service (SNAPCO$_2$, Paris, France) protocols (e.g., Corbière et al., 2007). From 15 certified Dickson standards (Batches #44 and #49, SCRIPPS, USA), an accuracy of ∼1.7 μmol kg^{-1} and, a reproducibility of ∼2.7 μmol kg^{-1}, based on 16 replicates, have been determined (Paulmier et al., 2008). O$_2$ samples were analysed according to the Winkler method, improved and adapted to low concentration detection (O$_2$ <40 μmol kg^{-1}) following Broenkow and Cline (1969), with an accuracy of 1 μmol kg^{-1} and reproducibility of 1.8 μmol kg^{-1} (Paulmier et al., 2006).

To validate results obtained from a local scale off Chile for the OMZs at the global scale (Paulmier and Ruiz-Pino, 2008), the DIC structure was determined in the permanent OMZs in the Tropical Pacific ocean (North – ETNP: Costa Rica, Mexico; South – ETSP: Peru) and Northern Indian ocean (Arabian sea – AS; Bay of Bengal – BB), in the seasonal OMZs in the West Bering Sea (WBS) and the Gulf of Alaska (GA), and in the Eastern Boundary Upwellings of the Atlantic Ocean (Canary and Benguela/Namibia). Globally, the study has been investigated mainly in the most intense OMZs in the Tropical Pacific and the Northern Indian Oceans with O$_2$ <20 μmol kg^{-1} in their core. The international databases GLODAP (GLobal Ocean Data Analysis Project; Sabine et al., 2005) for DIC and WOA2005 (World Ocean Atlas 2005; Boyer et al., 2006) for O$_2$ have been used. For a more consistent comparison between DIC and

O_2 data in terms of spatiotemporal coverage and sampling protocols, the analysis has been focused on the same cruises carried out during the WOCE program (World Ocean Circulation Experiment, www.coaps.fsu.edu/woce; >300 transects between 1992 and 1998). Indeed, the horizontal coverage by WOCE cruises measuring both DIC and O_2 (between 1992 and 1995, also in non El Niño years) is very similar in the main OMZ regions of the Pacific and Indian Oceans. Both accuracy and reproducibility of the data, respecting WOCE standards quality (WOCE Operation Manual, 1994) are: ~4 μmol kg^{-1} for DIC; ~2 μmol kg^{-1} (with a detection limit of ~10 μmol kg^{-1}) for O_2.

In addition, sensitivity tests on DIC and O_2 averages have been performed, taking into account the lower and upper vertical levels of the GLODAP and WOA2005 grids for each OMZ limit: 137.5 and 225 m for the upper limit (175 m); 850 and 1050 m for the lower limit (950 m). These tests have been summarized in Table 1 for the total OMZs, each OMZ and the global ocean. In general, the average DIC concentrations are more sensitive to the choice of the lower OMZ limit and in the ETNP (± 8 μmol kg^{-1}), where the DIC concentrations are the highest. On the contrary, the average O_2 concentrations are more sensitive to the choice of the upper OMZ limit, corresponding to the highest O_2 concentrations close to the saturation values. They are less sensitive in AS, with the lowest O_2 concentration on the thickest OMZ core. The maximal differences for both DIC and O_2, lower than the data accuracy + reproducibility (cf. above), suggest that the choice of the upper and lower OMZ limits for the determination of the associated DIC structure does not have a significant effect on the analysis proposed in the Results section here.

To compare the DIC increase versus O_2 decrease due to remineralization, which has been considered as the main mechanism responsible of the existence of all O_2 minima observed in the ocean (Wyrtki, 1962), an index is proposed:

$$\mathrm{DIC}^* = \mathrm{DIC} + 0.69\ \mathrm{O}_2 \tag{1}$$

0.69 = 117/170 is the stoichiometric carbon to oxygen ratio C/O of Anderson and Sarmiento (1994). It corresponds to the lowest and most commonly used C/O ratio value in the data analysis literature.

DIC* is defined as the sum of the observed DIC and DIC produced during remineralization by O_2 consumption. DIC* can be considered as an analogue of the nitrogen deficit index (e.g.: NO of Broecker, 1974; N* of Gruber and Sarmiento, 1997) or P* (Deutsch et al., 2007). DIC* should be conservative if no physico-chemical and/or biological mechanisms are affecting DIC and O_2 concentrations other than remineralization and/or photosynthesis with the same C/O stoichiometry. The accuracy and reproducibility of DIC and O_2 measurements lead to an accuracy and reproducibility for DIC* lower than 4.5 μmol kg^{-1}.

A water mass analysis based on an inverse method is performed to estimate the biogeochemical contributions for DIC production and O_2 consumption locally within the OMZ off Chile. This hydrological method (e.g., Minas et al., 1986) has already been described for O_2 in Paulmier et al. (2006) and detailed in Paulmier (2005). The contribution due to mixing processes has been determined by a correlation coefficient R^2 of ~0.9, using potential temperature and salinity as semi-conservative parameters. The measured DIC and O_2 concentrations can be expressed as the sum of a contribution due to mixing processes ($\mathrm{DIC}_{\mathrm{mixing}}$ and $\mathrm{O}_{2\ \mathrm{mixing}}$) and a contribution due only to biogeochemical processes called ΔDIC and ΔO_2 (the residuals). Positive or negative ΔDIC and ΔO_2 indicate (DIC and O_2) production or consumption, respectively. To compare the biogeochemical effect on O_2 of the OMZ communities at each sampled profile, we chose to apply our method locally to infer a local biogeochemical residual within the OMZ and in particular at the oxycline level. This implies a minor effect of the local horizontal mixing and advection which does not significantly affect the vertical $\mathrm{O}_{2\ \mathrm{mixing}}$ (Paulmier, 2005). The biogeochemical residuals can be interpreted as a resulting in situ DIC or O_2 consumption or production of the OMZ communities for each location, depth and period.

3 Results

DIC and O_2 datasets collected off Chile (Fig. 1) show a specific DIC structure associated with an OMZ already described in Paulmier et al. (2006). Then, in order to determine whether the description of the DIC structure detailed locally and temporally for the OMZ off Chile can be extended to the global scale, the representative DIC structure has been analysed globally in the main most intense OMZs.

3.1 Carbon maximum zone (CMZ) along the OMZ off Chile

The DIC structure, observed at 21° S from the shelf to off-shore (Iquique: Fig. 1a and c) but also at 30° S (Coquimbo: Fig. 1c; stations location in Fig. 1f), corresponds to a permanent structure off northern and central Chile. The DIC structure at 21° S shows low values (DIC<2140 μmol kg^{-1}) in surface, and a strong increase with depth from 20 m called carboncline (by analogy with the oxycline) up to maximal DIC concentrations (>2300 μmol kg^{-1}) on the continental shelf. The continental slope induces a 30–40 m shoaling of the carboncline (cf. DIC isolines between 2200 and 2275 μmol kg^{-1}) and of the maximal DIC (>2250 μmol kg^{-1}: in red-white, Fig. 1a). This shoaling follows the oxycline and OMZ core shoaling (cf. the 20 μM O_2 isoline, Fig. 1d). The DIC structure at 21° S (~2300 μmol kg^{-1} on average on the core) presents higher concentrations than at 30° S by ~50 μmol kg^{-1} (Fig. 1c), also associated with a less intense OMZ at Coquimbo from ~40 μmol kg^{-1} (Fig. 1f). At 36° S on the shelf (Concepcion Bay), DIC concentrations are much more variable than at 21° S and 30° S, with the highest concentrations reported

Table 1. Averaged DIC and O_2 concentrations in a mean layer intercepting the core of all main OMZs (175–950 m), and sensitivity tests (in italics; commented in §3.2) on upper (for 137.5 and 225 m) and lower limits (for 850 and 1050 m) from GLODAP and WOA2005 databases. Averages are given for tropical OMZs together (ETSP + ETNP + AS + BB) and separately, and for the global ocean. ETNP: Eastern Tropical North Pacific; ETSP: Eastern Tropical South Pacific; AS: Arabian Sea; BB: Bay of Bengal.

Averaged layer	175–950 m		137.5–950 m		225–950 m		175–850 m		175–1050 m		Maximal differencesin the 175–950 m layer	
Parameters (μmol kg^{-1})	DIC	O_2	DIC	O_2	DIC	O_2	DIC	O_2	DIC	O_2	DIC	O_2
Total OMZs	2284	22	2279	24	2289	20	2277	21	2289	23	*±7*	*±2*
ETSP	2285	22	2283	22	2287	22	2282	19	2288	26	*±3*	*±4*
ETNP	2286	24	2280	26	2292	22	2278	24	2292	25	*±8*	*±2*
AS	2276	12	2273	13	2279	12	2272	12	2280	13	*±4*	*±1*
BB	2278	20	2274	20	2281	20	2274	18	2282	22	*±4*	*±2*
	2203	157	2199	159	2208	155	2196	159	2209	155	*±7*	*±2*
Global ocean	Averages on the whole water column for:											
	DIC: 2255					O_2: 176						

off Chile (>2500 μmol kg^{-1} in spring 2000; Fig. 1b and c). The highest DIC concentrations (>2250 μmol kg^{-1}: in red, Fig. 1b) appear from the bottom (∼50 m depth) up to 10 m depth in austral spring-summer (October to March), associated with the OMZ establishing (O_2 <20 μM from 20 to 50 m in white: Fig. 1e). The DIC maximum (>2250 μmol kg^{-1}) starts to settle in spring during the high upwelling activity period, simultaneously with the OMZ core. In fall (April–May), the 2175 μmol kg^{-1} DIC isoline extends from 5 m near the surface to the bottom (Fig. 1b), indicative of a homogenized water column with lower DIC. It is coincident with the complete OMZ destruction (Fig. 1e). In the OMZ off northern and central Chile, the DIC maximum appears spatially and temporally collocated with the O_2 minimum of the OMZ core, despite differences in the OMZ intensity and shape between each site (Fig. 1f).

Considering all sampled data in the OMZ off Chile (Fig. 1), the whole DIC and O_2 profiles confirm a similar DIC structure associated with the OMZ: low concentrations in surface waters and an increase with depth, as in the oxygenated ocean (cf. classical profile out of the OMZ: Fig. 1c). However, on average, the observed increase off Chile is ∼5 times stronger than the usual increase. DIC concentrations reach values as high as 2330 ± 60 μmol kg^{-1} at 50–100 m. Usually for the same area but out of the OMZ, these high DIC are observed at 1000 m and deeper (WOCE 1992–95; Takahashi and Goddard, 1998). In addition, DIC concentrations in the OMZ off Chile remain high (>2250 μmol kg^{-1}) on the whole core thickness (O_2 minimum between 30 and 750 m). Thus, as compared with a representative classical DIC profile out of the OMZ, the OMZ off Chile presents a relative maximum of DIC (hatched in red: Fig. 1c). This DIC maximum, defined by $DIC_{CMZ} = DIC_{\text{Average on OMZ}} - DIC_{\text{Classical out of OMZ}}$, is called, by analogy with the OMZ, a carbon maximum zone (CMZ).

Although the CMZ defined here and the OMZ off Chile are relatively well correlated in terms of position and thickness, some differences appear, especially between the carboncline and the oxycline. The carbonclines start from the surface, at shallower depths than the oxyclines (from 5–10 m). In addition, the carbonclines are associated with some extreme DIC peaks (up to >2350 μmol kg^{-1}), whereas smooth low O_2 profiles can be observed at the oxycline.

3.2 Towards a validation of the CMZ existence at a global scale

The hypothesis of the CMZs existence at a global scale for all most intense OMZs is tested with GLODAP and WOA2005 datasets.

Vertically, the DIC distributions in the OMZs in the eastern tropical south and north Pacific (ETSP and ETNP), in the Arabian Sea (AS) and in the Bay of Bengal (BB), are low in surface (between 1900 and 2100 μmol kg^{-1}) and increase with depth up to 2300 μmol kg^{-1} (from Fig. 2a). As observed in the OMZ off Chile, all these OMZs present high DIC concentrations (always >2225 μmol kg^{-1}, Fig. 2a) over their core depths on average between ∼175 and ∼950 m depth (Fig. 2b). These high DIC concentrations in the OMZ cores are associated with a large DIC relative maximum, higher than 100 μmol kg^{-1} as compared to the global averaged DIC profile (continuous profile in Fig. 2a). These large DIC relative maxima suggest the existence of CMZs in all main OMZs, as defined for the OMZ off Chile.

The CMZs are the most intense in ETNP (DIC> 2300 μmol kg^{-1}) and the least intense in AS and BB, up to 150 μmol kg^{-1} and ∼100 μmol kg^{-1} higher than the average for the global ocean, respectively (Fig. 2a). This is likely a consequence of the higher accumulation of DIC along the Conveyer Belt in the ETNP CMZ than for the CMZs in the Northern Indian Ocean. In particular, the CMZ in BB

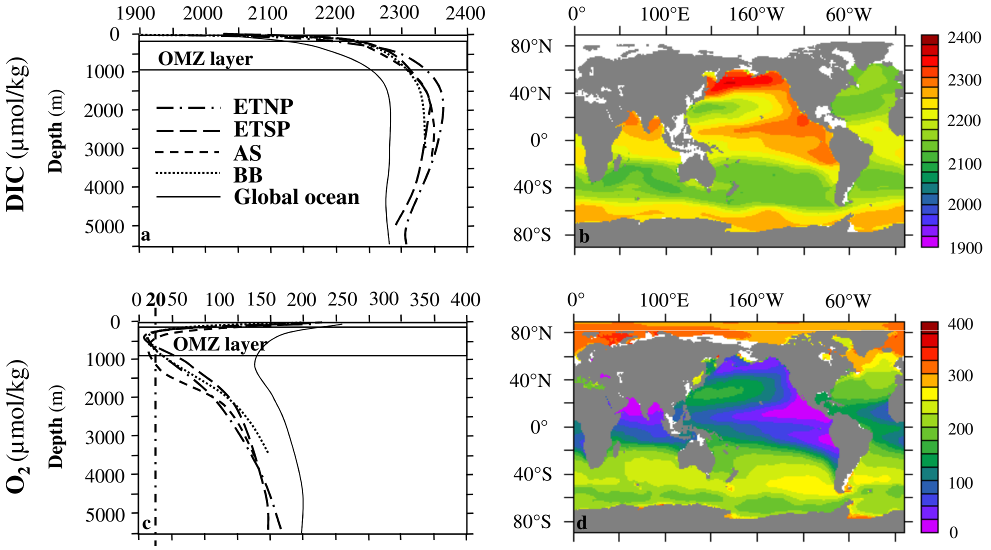

Fig. 2. Vertical profiles of DIC **(a)** and O_2 **(c)** on 0–5500 m for the main most intense OMZs in the open ocean from GLODAP and WOA2005 databases. The continuous profile in **(a)** and **(c)** corresponds to a mean global profile from the all available datasets both in and out the OMZs. Vertical dashed line in **(c)** corresponds to O_2 = 20 µmol kg^{-1} (upper O_2 concentrations of the OMZs core), and horizontal continuous lines in (**a** and **c**) correspond to the mean upper (175 m) and lower (950 m) depths of the OMZs core. Mean DIC **(b)** and O_2 **(d)** distribution average in µmol kg^{-1} on the 175–950 m, a layer intercepting the core of all main tropical OMZs (cf. Table 1). For ETNP, ETSP, AS and BB, same abbreviations than in Table 1 caption.

presents, for the whole regional bay, the lowest DIC concentrations near the surface (DIC≈1800 µmol kg^{-1} from the mean BB profile), probably due to the advection of important riverine freshwaters (e.g., Brahmaputra, Gange).

Horizontally, the analysis has been illustrated on DIC and O_2 fields over the 175 and 950 m layer, intercepting the core of all main tropical OMZs (Fig. 2b and d). The highest DIC concentrations (>2225 µmol kg^{-1}: in red-orange, Fig. 2b) are found in the tropical eastern north (ETNP) and south (ETSP) Pacific and northern Indian Oceans (AS; BB), and at high latitude around 60° N in the northern Pacific. These regions correspond to the most intense (O_2 <20 µmol kg^{-1}) OMZs and to the seasonal OMZs of the West Bering Sea and the Gulf of Alaska, respectively (in blue-purple, Fig. 2d). The Canary and Benguela upwelling systems and the China Sea, corresponding to the least intense O_2 minima (O_2 ≥40 µmol kg^{-1}: Karstensen et al., 2008; Chen et al., 1995; respectively) also correspond to high DIC (maxima around 2225 µmol kg^{-1}), albeit lower concentrations than for the Pacific and Indian OMZs. All main OMZs appear, thus, as potential CMZs. The reciprocal is not true, since the high DIC concentrations averaged between 175 and 950 m depth south of 50° S in the Southern Ocean (∼2250 µmol kg^{-1}) are not correlated with an OMZ. These high DIC concentrations are mainly associated with the deepest maximal mixed layer depths (≥250 m: De Boyer Montégut et al., 2004).

4 Discussion

The existence of CMZ, reported locally and temporally in the OMZ off Chile (Fig. 1), has been validated globally in all the main OMZs on both vertical mean profiles for each OMZ (Fig. 2a, c) and horizontal distribution (Fig. 2b, d). The CMZs-OMZs, because of the accumulation of high DIC (>2225 µmol kg^{-1}) in subsurface, constitute the largest reserves of carbon near the surface in the global ocean, ∼570 PgC, i.e., a comparable stock to the total atmospheric CO_2 content. This simple calculation is based on a mean DIC concentration of ∼2225 µmol kg^{-1}, reported over 940 m of the OMZ thickness between 10 and 950 m, multiplied by the total area of the tropical shallow OMZs (22.2 10^6 km^2: from Paulmier and Ruiz-Pino, 2008). The high DIC concentrations of ∼2225 µmol kg^{-1} are considered on both the carboncline-oxycline (10–175 m, as reported from local cruises: cf. Fig. 1c) and CMZ cores (175–950 m, as reported from global databases: cf. Fig. 2a). The existence of such CMZ explains why the OMZ can be an intense GHG oceanic local source of not only N_2O but also CO_2 (e.g., off Chile: Paulmier et al., 2008).

The mechanisms responsible for the carbon maximum structure (CMZ) associated with the OMZ are discussed. We will first examine the physico-chemical mechanisms inducing a differential CO_2 accumulation and deoxygenation in the CMZ-OMZ core. We will then focus our attention on more local and biogeochemical processes, associated with remineralization and carbon to oxygen molar ratio (C/O) at the carboncline-oxycline of the Chilean OMZ.

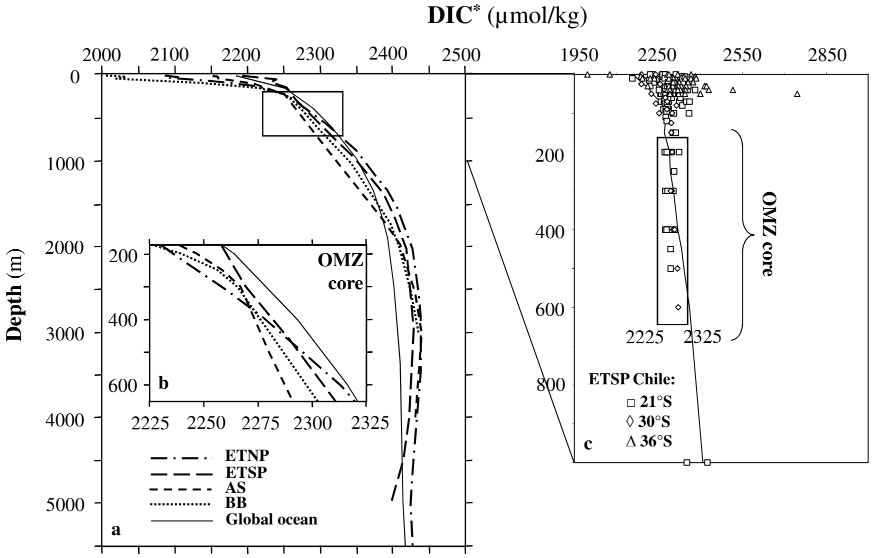

Fig. 3. Vertical profiles of DIC* (= DIC + 0.69 O_2: cf. Methodology and the comments provided for Eq. 1) for the main OMZs from GLODAP and WOA2005 databases on 0–5500 m **(a)**, with a zoom in the layer intercepting the core of all considered OMZs **(b)**, and from all stations sampled in the OMZ off Chile in 2000–2002 **(c)**. Continuous profile in (**a** and **c**) corresponds to a mean profile for the global ocean and for the oxygenated Pacific out of the OMZ, respectively. Rectangles in (**a** and **b**) indicate the OMZ core. For ETNP, ETSP, AS and BB, same abbreviations than in Table 1 caption.

4.1 Differential regional physico-chemical CO_2 accumulation and deoxygenation in the CMZ-OMZ core

It is in no way surprising to find DIC maxima associated with O_2 minima in subsurface, since remineralization degrading organic matter into CO_2 occurs mainly in subsurface layer and is classically aerobic, i.e., consuming O_2. CMZ in the OMZ is, thus, a logical consequence of remineralization end-products accumulation, agreeing with subsurface fields of nitrate, phosphate and silicate at the depth of the OMZ core. This accumulation of remineralization end-products is not distributed uniformly horizontally (Fig. 2b) and vertically (Fig. 2a). It mainly occurs in privileged zones, in particular the OMZs in the top 1000 m. The same dynamical mechanisms acting at different scales, already proposed for the OMZ formation (e.g., Paulmier and Ruiz-Pino, 2008; Karstensen et al., 2008), contribute to the CMZ formation. At a global scale, DIC accumulation occurs in the oldest waters, following the Conveyer Belt (Broecker and Peng, 1982) with the highest concentrations in Northern Pacific (the seasonal West Bering Sea and Gulf of Alaska OMZs). Low subsurface ventilation of shadow zones (Luyten et al., 1983) and confinement in regions surrounded by continents explain why CMZ-OMZs are located in the eastern Pacific and in the Northern Indian Ocean rather than in the Western Pacific and in the Southern Indian, respectively. The location of tropical shadow zones with older waters (10<100 years: Karstensen et al., 2008) explains why the DIC maximum and O_2 minimum are found in the equatorwards subsystems of the eastern boundary upwelling in both the Atlantic and Pacific Oceans. The upwelling activity (intensity; typology of cells: Endoh, 1976) and undercurrents transport (intensity, depth), as well as mixed-layer depth, affect the position of the CMZ-OMZs in subsurface (Paulmier and Ruiz-Pino, 2008). In particular, the upwelling explains why the DIC maximum starts shallower (<175 m) in the CMZ-OMZs than in the rest of the ocean on average (Fig. 2b, d).

However, despite similarities and co-localization of CMZ and OMZ, some differences appear. Let's assume that the dynamical transport and accumulation of DIC produced by remineralization is the only cause explaining the CMZ existence in an OMZ, then the DIC increase should be proportional to the O_2 decrease. The proportionality factor should be the C/O stoichiometric coefficient, if the molar C/O ratio of remineralization is constant. In this case, values of DIC* (= DIC + 0.69 O_2; Eq. 1) should be similar in the oxygenated ocean and in the OMZs. But, as illustrated in Fig. 3a–b, DIC* averages on OMZs core (DIC^*_{OMZ}) are slightly lower than the average on the global ocean (DIC^*_{Global}) for the same depth layer, by a significant difference of ∼10–20 µmol kg^{-1} ranging from 7 (ETNP) up to 25 (AS) µmol kg^{-1}. The DIC deficit in the global mean CMZ-OMZ core thickness is much clearer for the AS CMZ around 1000 m deep since the AS OMZ core is ∼20% deeper than the other OMZ cores (Paulmier and Ruiz-Pino, 2008). Anyway, this difference is higher than DIC* uncertainty (cf. Methodology). This difference suggests that the CMZ core exhibits a slight DIC deficit compared to the DIC expected maximum, i.e., the DIC produced by a remineralization (Re)

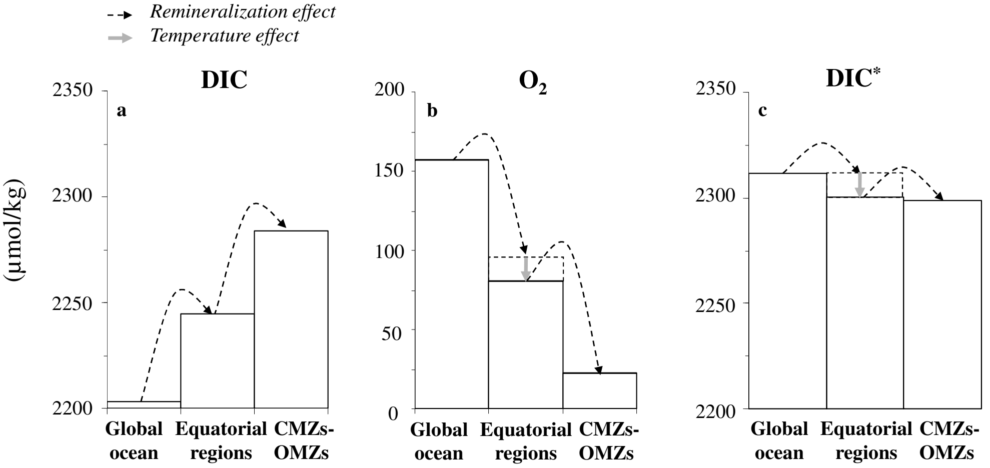

Fig. 4. DIC **(a)**, O_2 **(b)** and DIC* **(c)** mean concentrations for global ocean, equatorial regions (Indian and Pacific only, where the main intense OMZs are located; between 10° N and 10° S; between 175 and 950 m, in the same depth layer than the subsurface OMZ core), and CMZs-OMZs. In dashed arrows, the remineralization effect from the global ocean towards the Equatorial regions and the CMZs-OMZs. In thick grey arrows, the temperature effect mainly decreasing the solubility, not visible on DIC **(a)** because of the buffer effect, but on O_2 **(b)** and DIC* **(c)** only.

consuming the entire O_2 amount necessary to form the OMZ and following the chosen constant C/O stoichiometry. Estimating a DIC_{Re} of ∼93 μmol kg^{-1} (=0.69*(157–22) from $O_{2\ OMZ}$ = 22 μmol kg^{-1} and $O_{2\ \mathrm{Global\ ocean}}$ = 157 μmol kg^{-1}; Table 1), the DIC deficit is accounting around >10% of the total DIC produced by remineralization. Note that for all DIC* calculations presented here, sensitivity tests were performed, especially with a higher C/O value (the canonical C/O = 106/138 from Redfield et al., 1963). These tests did not change the conclusions.

Theoretically, the history of the water masses which give origin to the CMZ-OMZ will affect the DIC and O_2 values in addition to the strict biological effect. Water masses forming the CMZ-OMZs cores come from surface equatorial and/or tropical warm waters. In the Pacific, CMZs-OMZs waters mainly originate from the Pacific equatorial waters advected through zonal equatorial undercurrents (e.g., Tsuchiya, 1981; Karstensen et al., 2008): (i) from the Equatorial SubSurface Water through the Peru-Chili undercurrent (PCU) for the ETSP (Strub et al., 1998; Paulmier et al. 2006); (ii) from the SubTropical Underwater Water formed near the Equator for the ETNP (O'Conner et al., 2002; Maske et al., 2010). The AS CMZ-OMZs waters originate from the Red Sea and Persian Gulf (Morrison et al., 1999) and the BB subsurface waters come from the surface equatorial Indian ocean (Rao et al., 1996; Sarma et al., 1998). The equatorial regions are net O_2 sinks, despite a thermal O_2 source effect (Najjar and Keeling, 2000), which tends to diminish the surface O_2 concentration, thereby affecting DIC*. Since DIC* = DIC + 0.69 O_2, a decrease of DIC* is expected in the warm regions due to the higher temperature lowering the gas solubility. Indeed, an increase of temperature from 15° to 25 °C, corresponding to the mean subsurface and surface temperatures for tropical and equatorial regions, and for a standard mean salinity of 35 (CARS database, 2009), would decrease the O_2 solubility by >10% (Weiss, 1970). A similar additional effect is occurring on dissolved CO_2 (Weiss, 1974), but it remains negligible because of the buffer effect due to the CO_2 dissociation (<1%; Lewis and Wallace, 1998).

The global dataset analysis confirms that the differential CO_2 accumulation and deoxygenation is occurring upstream in the regions where the CMZs-OMZs water are pre-formed, mainly in the equatorial regions (Fig. 4). In the subsurface layer (175–950 m) corresponding to the CMZs-OMZs depths, DIC* is decreasing from the global ocean to the equatorial regions by ∼10 μmol kg^{-1} (Fig. 4c), whereas DIC* is similar in the CMZs-OMZs and in equatorial regions. For Chile, OMZ DIC and O_2 concentrations in PCU confirm this result, since PCU is advecting waters poorer in O_2 (Paulmier et al., 2006) than richer in DIC, inducing a lower DIC*. The differential thermal effect on DIC and O_2 is needed to explain why DIC* decreases from the global ocean (GO) to Equatorial regions (ER), from a DIC* value of 2311 μmol kg^{-1} to a DIC* value of 2300 μmol kg^{-1} (Fig. 4c). Let us use the DIC* definition and the decomposition of DIC*, DIC and O_2 into the physical and biogeochemical components. Let us assume that the thermal effect (Th) and remineralization (Re) can be associated with the physical and biogeochemical components in subsurface waters, respectively.

$$\mathrm{DIC}^*_{\mathrm{GO}} - \mathrm{DIC}^*_{\mathrm{ER}} = (\mathrm{DIC}^*_{\mathrm{GO\ Th}} + \mathrm{DIC}^*_{\mathrm{GO\ Re}})$$

$$- (\mathrm{DIC}^*_{\mathrm{ER\ Th}} + \mathrm{DIC}^*_{\mathrm{ER\ Re}})$$

Because $\mathrm{DIC}^*_{\mathrm{GO\ Re}} - \mathrm{DIC}^*_{\mathrm{ER\ Re}} = 0$ by definition,

$$\mathrm{DIC}^*_{\mathrm{GO}} - \mathrm{DIC}^*_{\mathrm{ER}} = \mathrm{DIC}^*_{\mathrm{GO\ Th}} - \mathrm{DIC}^*_{\mathrm{ER\ Th}}$$

$$= (\mathrm{DIC}_{\mathrm{GO\ Th}} + 0.69\ \mathrm{O}_{2\ \mathrm{GO\ Th}})$$

$$- (\mathrm{DIC}_{\mathrm{ER\ Th}} + 0.69\ \mathrm{O}_2\ \mathrm{ER\ Th})$$

$$= (\mathrm{DIC}_{\mathrm{GO\ Th}} - \mathrm{DIC}_{\mathrm{ER\ Th}}) + 0.69\ (\mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}})$$

Considering here $\mathrm{DIC}_{\mathrm{GO\ Th}} - \mathrm{DIC}_{\mathrm{ER\ Th}} \approx 0.01$ ($\mathrm{CO}_{2\ \mathrm{GO\ Th}}$ – $\mathrm{CO}_{2\ \mathrm{ER\ Th}}$) with a constant CO_2 buffer effect of 1% and a negligible temperature effect on this Revelle factor of 0.01 (Lewis and Wallace, 1998), and assuming $\mathrm{CO}_{2\ \mathrm{GO\ Th}}$ – $\mathrm{CO}_{2\ \mathrm{ER\ Th}} \approx \mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}}$ (similar solubility variation for CO_2 and O_2):

$$\mathrm{DIC}^*_{\mathrm{GO}} - \mathrm{DIC}^*_{\mathrm{ER}} = 0.01(\mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}})$$

$$+0.69\ (\mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}})$$

$$= 0.70\ (\mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}})$$

With $\mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}}$

$$= (\mathrm{O}_{2\ \mathrm{GO}} - \mathrm{O}_{2\ \mathrm{ER}}) - (\mathrm{O}_{2\ \mathrm{GO\ Re}} - \mathrm{O}_{2\ \mathrm{ER\ Re}}) \text{ and}$$

$$(\mathrm{O}_{2\ \mathrm{GO\ Re}} - \mathrm{O}_{2\ \mathrm{ER\ Re}}) = -(\mathrm{DIC}_{\mathrm{GO\ Re}} - \mathrm{DIC}_{\mathrm{ER\ Re}})/0.69 \approx$$

$$-(\mathrm{DIC}_{\mathrm{GO}} - \mathrm{DIC}_{\mathrm{ER}})/0.69$$

$$\mathrm{O}_{2\ \mathrm{GO\ Th}} - \mathrm{O}_{2\ \mathrm{ER\ Th}} = (\mathrm{O}_{2\ \mathrm{GO}} - \mathrm{O}_{2\ \mathrm{ER}})$$

$$+(\mathrm{DIC}_{\mathrm{GO}} - \mathrm{DIC}_{\mathrm{ER}})/0.69 = 77 - 61/0.69$$

$$= 16\ \mu\mathrm{mol kg}^{-1}$$

(from the dashed arrows: Fig. 4a–b), and $\mathrm{DIC}^*_{\mathrm{GO}}$ – $\mathrm{DIC}^*_{\mathrm{ER}}$ = 0.70×16≈11 µmol kg^{-1} as expected from the direct calculation.

Therefore, the temperature effect on the solubility appears to be the mechanism decreasing the O_2 concentration in the CMZs-OMZs originating regions, and mainly driving and explaining the slightly lower DIC* observed in the CMZs-OMZs (Fig. 3). In particular, the faster air-sea exchanges for O_2 than for CO_2 should explain why carbonclines start slightly shallower (by 5–10 m) than oxyclines, in addition to the photosynthesis effect in surface depleting more DIC than the supersaturating O_2 (e.g., Minas et al., 1986). Our approach only demonstrates that a DIC deficit (DIC* <$\mathrm{DIC}^*_{\mathrm{Global}}$) could be due to physico-chemical mechanisms prior to the complete CMZ-OMZ formation, since dynamical connection between equatorial waters and OMZ cores is complex, indirect and still not very well known.

4.2 Local remineralization and biogeochemical C/O variations at the carboncline-oxycline

In addition to regional physico-chemical contribution to the DIC deficit of the CMZ-OMZ core, specific local mechanisms could affect C/O in OMZs and, thus, help to explain why $\mathrm{DIC}^*_{\mathrm{OMZ}}$ is different from $\mathrm{DIC}^*_{\mathrm{Global}}$. Off Chile (Fig. 3c), the CMZ-OMZ core also presents a DIC* (∼2225 µmol kg^{-1}) lower than in oxygenated waters, by a difference up to ∼60 µmol kg^{-1} and ∼20 µmol kg^{-1} on average similar to those discussed from the global dataset (Fig. 3a–b). On the contrary, above the core, at the carboncline-oxycline depths between 10 and 175 m depending on the site, $\mathrm{DIC}^*_{\mathrm{Chile}}$ is much higher by ∼80 µmol kg^{-1} on average than in oxygenated waters and in the core (Fig. 3c). The highest variability (up to ∼750 µmol kg^{-1}) and concentrations (DIC* >2500 µmol kg^{-1}) correspond to 36° S (Fig. 3c), the shallowest site on the continental margin associated with a seasonal CMZ-OMZ (Fig. 1 b and e). The variation of DIC* can be due to the local deviation of the C/O in the CMZ-OMZ from the fixed value chosen for the global scale analysis. Indeed, a plot of (DIC) over (O_2) for the global ocean (85 650 data points from the WOCE cruises; Fig. 5a) indicates that a linear regression leads to a slope of 0.7 very close to C/O = 0.69 (Anderson and Sarmiento, 1994) chosen for our DIC* computation. This plot strongly presents higher and lower deviations from a linear regression, indicated by a low coefficient $R^2 = 0.25$. Thus, we investigated for local C/O deviations, especially at the carboncline-oxycline. To study the potential influence of the high remineralization on DIC production contributing to the CMZ formation, we evaluated the biogeochemical DIC production. Results of the hydrological method provide generally positive Δ DIC = $\mathrm{DIC}_{\mathrm{measured}}$-$\mathrm{DIC}_{\mathrm{mixing}}$, indicating a net “new” DIC production by biogeochemical processes (Fig. 1c), in opposition with an “old” DIC advected in the CMZ-OMZ. Note that this approach provides a time-integrated information for the biogeochemical contribution to DIC concentration: Δ are expressed in terms of concentration (µmol kg^{-1}), and not in terms of rate.

In this study, no direct in situ measurement of any bacterial activity has been performed along the Chile OMZ allowing to identify microbial organisms and to prove the existence of biogeochemical processes. However, from theoretical stoichiometric equations for the known biogeochemical processes, although under-constrained and taking into account the uncertainties in the inverse method, it is possible to detect the “signature” of different dominant processes on both DIC and O_2. For example, aerobic remineralization produces DIC (ΔDIC>0) and consumes O_2(ΔO_2 <0), and inversely for photosynthesis. Anaerobic remineralization (e.g., denitrification, or even DNRA) produces DIC (ΔDIC>0) without consuming O_2(ΔO_2 ≈0) by definition. Bacteria involved in the autotrophic processes such as nitrification and anammox should consume DIC (carbon source for assimilation;

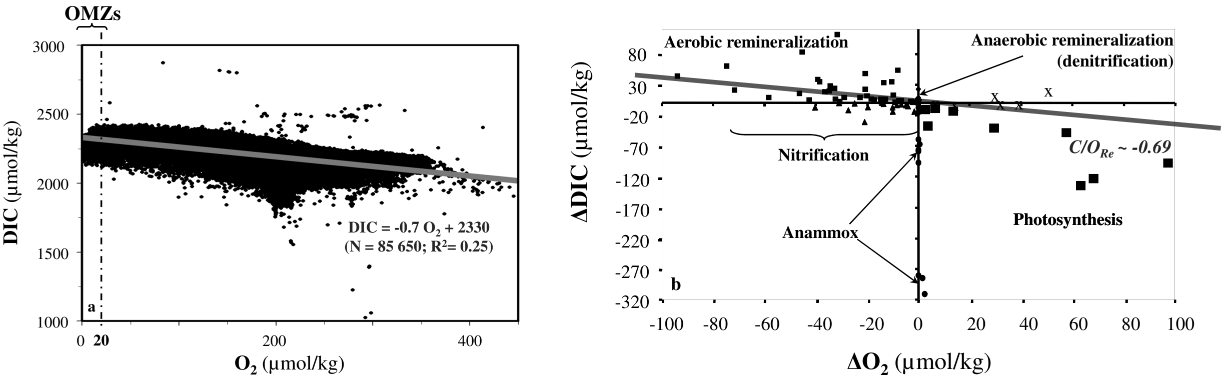

Fig. 5. **(a)**: DIC-O_2 diagram for the global ocean (all WOCE data with both DIC and O_2 available). **(b)**: ΔDIC- ΔO_2 diagram (from all stations sampled in the OMZ off Chile in 2000–2002, mainly focused in the oxycline). For **(a)**, the grey line corresponds to classical linear regression, with N = 85 650 data and a regression coefficient R^2 of 0.25: DIC = −0.7 O_2 + 2330. For **(b)**, ΔDIC and ΔO_2 correspond to the biogeochemical contribution to DIC and O_2, respectively, using an inverse method (cf. Methodology). Each symbol corresponds to one dominating biogeochemical process, which has been suggested and identified indirectly from theoretical chemical reactions: aerobic remineralization (small squares); nitrification (triangles); anaerobic remineralization (diamonds, mainly near ΔDIC-$\Delta O_2 \approx$(0,0)); photosynthesis (large squares); anammox (circles). Crosses correspond to non determined process. Accuracy and reproducibility on DIC and O_2 induce an uncertainty on the Δ of ∼4 µmol kg^{-1} (cf. Paulmier et al., 2006). $(C/O)_{Re}$ corresponds to the reference molar ratio for this study of 117/170 (Anderson and Sarmiento, 1994).

ΔDIC<0), but do ($\Delta O_2 <0$) and do not ($\Delta O_2 \approx 0$) consume O_2 as aerobic and anaerobic process, respectively. All computed (ΔDIC, ΔO_2) for our sampling off Chile are reported in the carboncline-oxycline (Fig. 5b) where DIC^*_{Chile} appears the highest and most variable. Here, the ΔDIC-ΔO_2 diagram (Fig. 5b) can only provide qualitative information, since each point corresponds to the predominance of a given process, and a large spatiotemporal variability is expected (e.g., between shelf and open ocean). Each situation corresponding theoretically to one dominant identified biogeochemical process (Fig. 5b) has been already observed off Chile and/or in other global OMZs. Indeed, for the same sites and/or periods off the Chilean OMZ, denitrification (Graco, 2002), anammox (Thamdrup et al., 2006; Galán et al., 2009) and nitrification (Molina et al., 2007) were observed to occur and tend to confirm the results of our simple biogeochemical approach. The reported (ΔDIC, ΔO_2) correspond to a net biogeochemical contribution, which is the net result of different superimposed processes. In particular, the situations (ΔDIC>0, $\Delta O_2 >0$), because of unknown biogeochemical process, could be interpreted as the superimposition of remineralization processes and photosynthesis. One needs to be very cautious concerning the indirect anammox detection, because anammox would correspond to two groups of (ΔDIC, ΔO_2) points: ΔDIC≈ −70 µmol kg^{-1}, and ≈ −300 µmol kg^{-1}. Note also that DIC and O_2 can be affected not only by biogeochemical processes occurring in the water column, but also by sedimentary mechanisms (respiration), particularly active off the semi-enclosed Bay of Concepción as early diagenesis (e.g., Graco, 2002). Especially in non El Niño periods, bottom waters are influenced by a benthic organic remineralization (e.g., Graco et al., 2006) and then could produce DIC.

Net heterotrophy (remineralization) appears to be coexistent with net autotrophy (e.g., mainly nitrification but also anammox and photosynthesis: Fig. 5b), as suggested by chemolithoautrophic evaluations for the same sampling location than this study at 36° S (Farías et al., 2009). However, net heterotrophy (ΔDIC>0) corresponds to most situations (>50% of the points in Fig. 5b), compared to net autotrophy (ΔDIC<0). In aerobic configurations ($\Delta O_2 <0$), net heterotrophy would induce higher DIC production versus O_2 consumption than expected from reference C/O_{Re} ratio, with mainly 110> ΔDIC>40 µmol kg^{-1}, whereas net autotrophy corresponds mainly to −40< ΔDIC<0 µmol kg^{-1}. This suggests a potential predominance of heterotrophy versus autotrophy for ΔDIC, which would lead to higher C/O at the oxycline, and explaining the high $DIC^*_{Chile\ Oxycline}$ compared to the oxygenated ocean reported in Fig. 3c. This heterotrophy predominance would also be associated with predominance of net aerobic (the highest ΔDIC correspond to the most negative ΔO_2: <20 µmol kg^{-1}) over net anaerobic (anammox and denitrification with low ΔDIC: <40 µmol kg^{-1} on axis $\Delta O_2 = 0$) activity (Fig. 5b). Referring to Paulmier et al. (2006), heterotrophy and autotrophy would correspond to active and passive OMZ phases, with high ($|\Delta O_2| >20$ µmol kg^{-1}) and low ($|\Delta O_2| <20$ µmol kg^{-1}) O_2 consumption, respectively. The transition from active to passive phases suggests the importance of a potential coupling between mechanisms for C/O variations: heterotrophic-autotrophic (e.g., remineralization-photosynthesis); aerobic-anaerobic (e.g., aerobic remineralization-denitrification; nitrification-anammox, cf. Lam et al., 2007); but also photic-aphotic (photosynthesis-nitrification). Local high DIC production contributing to CMZ formation (ΔDIC up to 110 µmol kg^{-1})

would be associated with high O_2 consumption, stimulated by O_2 availability in the oxycline rather than surface biomass availability (Paulmier et al., 2006). This DIC production would be encouraged by specific characteristics of the shallow oxycline (e.g., large range of O_2 concentrations; well-lit; stratified) allowing a potential co-existence of different bacterial processes (Fig. 5b) which usually do not occur at the same depth. This high DIC production could be also associated with a sedimentary potential effect and with possible effect of carbonate dissolution as an additional DIC source. In fact, together with high particulate organic matter sinking along these productive areas, calcium carbonate may also be produced in the euphotic layer (e.g., coccolithophorids in the upwelling regions: Giraudeau et al., 1993). The high DIC in the OMZ may, thus, be produced not only by high organic carbon remineralization but also probably by relatively high carbonate dissolution. The carbonate dissolution could be higher within than outside of the OMZs due to both growth of calcifying plankton (e.g., coccolithophorids and foraminifera) in the euphotic layer and high dissolution favoured in the subsurface (Wollast and Chou, 1998). These different hypotheses have to be tested, since, as for O_2 consumption, intense DIC productions estimated at the oxycline agree with previous works in configurations of oxic-anoxic oscillation (e.g., Abril et al., 1999, 2010) and other experimental works (e.g., Sun et al., 2002). In addition to the net heterotrophy of the suboxic OMZ core, demonstrated by Koeve and Kähler (2010), the oxycline would highly contribute to the CMZ formation.

DIC production and consumption at the oxycline can affect C/O molar ratios but also C/N ratios. Here, $\Delta\mathrm{DIC}/\Delta\mathrm{O}_2$ corresponds to drawdowns from a superimposition of several processes with different molar biomass ratio. $\Delta\mathrm{DIC}/\Delta\mathrm{O}_2$ do not exactly correspond to strict C/O Redfield ratios (RR) determined in organic matter, but provide a first C/O approximation according to the Redfield definition linking molar ratios to biological processes (Redfield et al., 1963). In the oxycline, we have $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{O}_2|_{\mathrm{max}}$ varying from 0.6 to 1.5, and $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{NO}_3^-|_{\mathrm{max}}$ varying from ~0 to 16, quite concomitantly (data not shown). $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{O}_2|_{\mathrm{max}}$ and $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{NO}_3^-|_{\mathrm{max}}$ differ from the classical canonical RR of $106/138 \approx 0.8$ and $106/16 \approx 6.6$, respectively. On average for the whole dataset in the oxycline off Chile, $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{O}_2|_{\mathrm{max}}$ (1.1 ± 0.3) are twice as high as the RR, and $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{NO}_3^-|_{\mathrm{max}}$ (8.4 ± 4.5) is 20% higher than RR.

In OMZs, anomalous low N/P (<10 instead of 16) have been classically reported as, for example, off Peru (Codispoti and Christensen, 1985). Abnormally high C/O of ~1.1 (Millero et al., 1998) and C/N of 7–8 (Graco, 2002) have already been observed as well, but in iron fertilization experiment (IRONEX II, Indian Ocean) and anoxic sediments (on the shelf off Chile), respectively. The OMZ specific remineralization associated with the coexistence of different bacterial processes should be a key-element to understand why $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{O}_2|_{\mathrm{max}}$ ratio in the carboncline-oxycline is abnormally variable. High ΔDIC and $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{O}_2|_{\mathrm{max}}$ could theoretically and locally result from higher rates of DIC production. They could also derive from a more complete degradation of highly carbonated organic matter (OM) and different OM stoichiometries (cf. Van Mooy et al., 2002; Paulmier et al., 2009). Abnormality of $|\Delta\mathrm{DIC}|_{\mathrm{max}}/|\Delta\mathrm{O}_2|_{\mathrm{max}}$ molar ratios reported here in the OMZ off Chile suggests a perturbation of the ecosystem as compared to the oxygenated ocean, and could provide some information about molar ratios of the primitive anoxic ocean.

5 Conclusions

This study has shown that the OMZ off Chile is associated with very high DIC concentrations (mean of $2330 \pm 60\,\mu\mathrm{mol\,kg^{-1}}$) at depths from ~175–950 m. These high DIC concentrations, corresponding to a local DIC maximum as compared to the oxygenated ocean, allow us to define a carbon maximum zone (CMZ) over the whole OMZ thickness, including a carboncline associated with the oxycline. At a global scale, all OMZs form CMZs ($\mathrm{DIC} > 2225\,\mu\mathrm{mol\,kg^{-1}}$), with comparable vertical and horizontal structures and similar biogeochemical characteristics.

The existence of CMZs associated with all OMZs suggests that remineralization and/or accumulation of remineralized end-products are not uniformly distributed, but mainly occur in the OMZs. CMZ and OMZ are probably forming simultaneously with the same dynamical (low ventilation and upwelling) and biogeochemical (remineralization producing DIC and consuming O_2) mechanisms. However and paradoxically, CMZs exhibit a "carbon deficit" (DIC*) in their core of ~10% of the remineralized DIC. This "carbon deficit" can be related to the physico-chemical (thermal effect) genesis of CMZ-OMZ core from upstream (e.g., equatorial) waters. Locally, the "carbon deficit" in the CMZ core appears to be compensated by a "carbon excess" at the carboncline-oxycline, induced by an intense aerobic-anaerobic remineralization. This specific remineralization is due to a potential net heterotrophic co-existence of different bacterial processes usually occurring at different depths. This co-existence contributes to a shallow and strong CO_2 production easy to be released toward the atmosphere, and may induce C/O ratio deviation from canonical Redfield ratios. However, if OMZs are associated with high remineralization activity, phytoplankton in surface could benefit from an "OMZ-regenerated" primary production after an upwelling episode, inducing a negative feedback effect on the oceanic CO_2 release. Indeed, OMZs highly recycle nutrients such as phosphates and silicates, much less nitrate due to denitrification and anammox. Reduced conditions created in OMZs could also be favourable to greater bio-availability for metals such as iron.

The existence of the CMZs-OMZs would imply anomalous molar ratios, which remain to be confirmed for all main OMZs. High DIC, associated with relatively low alkalinity (∼2325 µeq/kg) and the predominance of aerobic remineralization and nitrification, would largely acidify the OMZ core waters. This acidification would induce perturbations of marine biogeochemistry and ecosystems in addition of the respiratory barrier due to the O_2 deficit. CMZs-OMZs can be considered as "natural laboratories" of a low O_2 and already "high CO_2" ocean. They are ideally suited for studies looking back in the past and aiming to predict the future, as planned in international programs, such as SOLAS (Surface Ocean Lower Atmosphere Study) mid-term strategies.

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