

## Carbon dioxide system in the Canary region during October 1995\*

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**SUMMARY:** During the cruise F/S Poseidon 212/3 (September 30-October 8, 1995) determination of carbon system variables was carried out over the section of La Palma-La Graciosa and at the ESTOC station in the Canary Island area. Total alkalinity and pH in the total scale at 25°C were determined at 24 stations from surface to bottom. In this area, the presence of different water masses can be traced by the carbon system variables. NACW is defined by a strong gradient of  $A_T$  and pH from 150 to 750 m. MW is characterised by high values of  $A_T$  and pH between 1000 to 1200 m and AAIW signals are found at around 900 m in the strait between Gran Canaria and Fuerteventura with low  $A_T$ , low pH and a maximum of  $fCO_2$ . Assuming an atmospheric mean value of  $fCO_2$  of 360  $\mu\text{atm}$  and an average surface value of  $393 \pm 7 \mu\text{atm}$ , we can conclude that during this cruise this oceanic area tends to release  $CO_2$  into the atmosphere, acting as a weak source with a carbon flux towards the atmosphere of  $+8.0 \pm 1.8 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ . The saturation levels in the Canary Island area have been found to be higher than 3600 m for calcite and 2700 m for aragonite. The inorganic carbon/organic carbon ratio (IC/OC) varies from 0.07 at 300 m to 0.5 at 3000 m. The IC/OC ratio shows that about a 34% increase in the  $C_T$  of the deep water is contributed by the inorganic  $CaCO_3$  dissolution. The IC at 300 m is around  $7 \mu\text{mol kg}^{-1}$ , increasing with depth to  $37.5 \mu\text{mol kg}^{-1}$  at 3700 m.

**Key words:** carbonate system,  $pH_T$ , total alkalinity, total inorganic carbon,  $CO_2$  fugacity.

### INTRODUCTION

The carbonate system in seawater is one of the most complex topics in oceanography. The system has long interested many oceanographers from various fields since it plays an important role in the biogeochemical cycles of three sub-spheres of the Earth, the biosphere, the lithosphere, and the hydrosphere (Chen and Wang 1995). More recently, the fate of fossil fuel  $CO_2$  has promoted interest in the study of carbonate chemistry in the oceans, because of the

greenhouse effect of carbon dioxide on the global climate. Oceanic uptake is a key part of the global budget of the  $CO_2$  released into the atmosphere by human activities. Present estimates indicate that about 40% of the anthropogenic  $CO_2$  added to the atmosphere due to the burning of fossil fuels is absorbed by the oceans (Post *et al.*, 1990; Houghton *et al.*, 1995). The capacity of the oceans for uptake of  $CO_2$  depends on the inorganic carbon chemistry and also depends greatly on many factors such as hydrography, circulation of water masses, mixed-layer dynamics, wind stresses and the biological processes in the ocean (Broecker and Peng, 1982).

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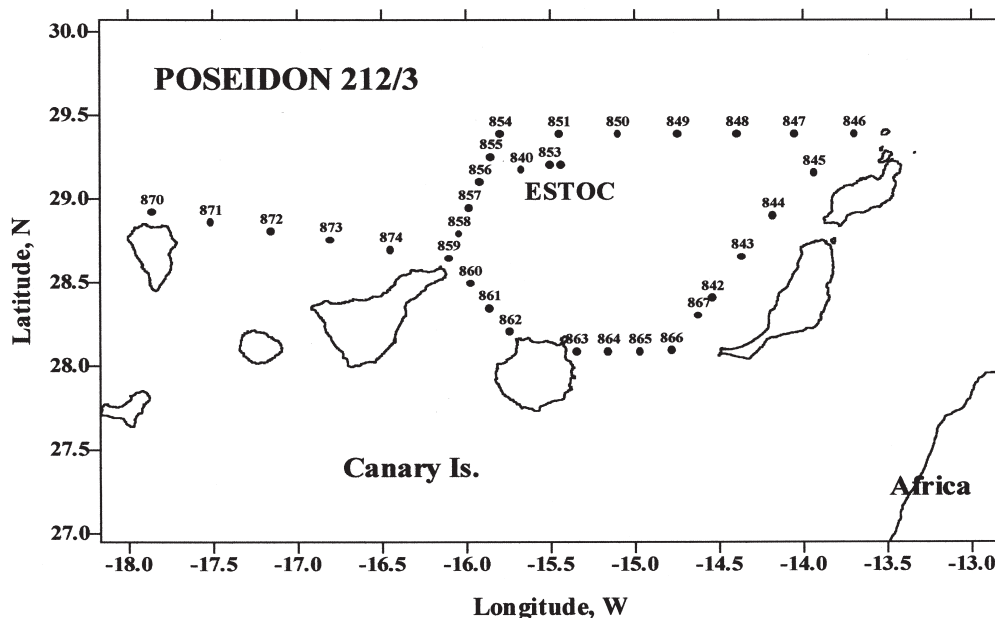


FIG. 1. – The Northeast Atlantic Ocean at the Canary Islands and stations grid for POSEIDON 212/3 cruise (September 30 - October 8, 1995).

The North Atlantic, with oceanic high latitude regions of deep water formation, mid-latitude sites of mode water formation and subtropical oligotrophic oceans, is thought to be a large sink for atmospheric CO<sub>2</sub> (Tans *et al.*, 1990; Takahashi *et al.*, 1993, 1995). The Canary Oceanic region (Fig. 1) is situated in a peculiar area 100-600 km west of the NW African coast in the eastern extensions of the subtropical North Atlantic gyre at a latitude of 27-28°N. It is part of the recirculation regime linking the Gulf Stream with the North Equatorial Current via the Azores and Canary Currents (Stramma and Siedler, 1988, Klein and Siedler, 1989). The structure of the Canary Current System is strongly influenced by the seasonally varying trade winds and the resulting upwelling regime off North-West Africa (Stramma and Siedler, 1988). The thermohaline properties of water masses involved in the water column in the Eastern North Atlantic have been extensively described in previous studies (Broecker and Takahashi, 1981, Arhan *et al.*, 1994, Measures *et al.*, 1995). Below North-Atlantic Central Water (NACW), the penetration and influence of both Antarctic Intermediate Water (AAIW) at around 900 m and Mediterranean Water (MW) between 900 and 1500 m are clearly observed in the North Atlantic (Fig. 2a).

During the Poseidon 212/3 cruise (30 September-8 October 1995), the determination of carbon system variables was carried out north of the Canary Islands between La Palma and La Graciosa. Total

alkalinity and pH at total scale and at 25°C were determined at 24 stations from surface to bottom. The main objective of this work was to study for the first time the carbon cycle in this area in order to evaluate the capacity of the zone for removing anthropogenic carbon dioxide from the atmosphere and to calculate both the saturated state of CaCO<sub>3</sub> and the ratio of in situ inorganic and organic carbon decomposition (IC/OC).

## EXPERIMENTAL

### pH

The pH in total scale (mol kg<sup>-1</sup>) was measured at 25°C using the potentiometric technique. The electrodes used to measure the e.m.f. of the sample consisted of a ROSS glass pH electrode and an Orion double junction Ag/AgCl reference electrode, connected to an Orion 720A pH meter. The electrodes were calibrated using a TRIS/HCl buffer in synthetic seawater with a salinity of 35 and corrected following the last recommendations by DelValls and Dickson (1998) and Lee *et al.* (2000). The tris buffer and the seawater samples were measured at 25°C, which allows the e.m.f. of the pH cell to be measured, first in the tris buffer and then in the seawater sample. The pH of the unknown seawater samples was determined according to standard operating procedures (Dickson and Goyet, 1994).

Repeatedly, seawater measurements of different CRM (certified reference material) samples (n = 54) gave a standard deviation of  $\pm 0.003$  pH units.

### Total alkalinity

The total alkalinity of seawater ( $A_T$ ) was determined by titration with HCl to the carbonic acid end point using two potentiometric systems and described in more detail in Mintrop *et al.* (2000). The HCl solution (25 l, 0.25 M) was made from concentrated analytical grade HCl (Merck®, Darmstadt, Germany) in 0.45 M NaCl, in order to yield an ionic strength similar to open ocean seawater. The acid was standardised by titrating weighed amounts of  $\text{Na}_2\text{CO}_3$  dissolved in 0.7 M NaCl solutions. The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point,  $\text{pH}_{\text{equiv}} = 4.5$ , according to the exact definition of total alkalinity (Dickson, 1981). The performance of the titration systems was monitored by titrating different samples of certified reference material (CRM, batch #35) that have known inorganic carbon and  $A_T$  values. The agreement between our data and certified values was within  $\pm 1.5 \mu\text{mol kg}^{-1}$ .

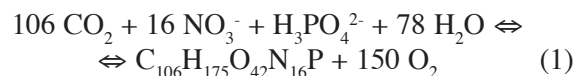
### Total inorganic carbon and $f\text{CO}_2$

Total inorganic carbon ( $C_T$ ) and  $f\text{CO}_2$  were computed from experimental values of  $\text{pH}_t$  and total alkalinity using the carbonic acid dissociation constants of Dickson and Millero (1987) following the last suggestions by Lee *et al.* (2000). Considering the accuracy of potentiometric pH ( $\pm 0.005$ ) and potentiometric total alkalinity ( $\pm 1 \mu\text{mol kg}^{-1}$ ) determinations (Mintrop *et al.*, 2000), the accuracy of  $C_T$  and  $f\text{CO}_2$  values are  $\pm 4 \mu\text{mol kg}^{-1}$  and  $\pm 5 \mu\text{atm}$ , respectively (Millero, 1995; Lee *et al.*, 1997).

## RESULTS AND DISCUSSION

### pH and alkalinity vertical profiles

Seawater pH reflects the status of the carbon dioxide system, which provides the major short-term pH buffer. In turn, the carbonate system is intimately linked with biological productivity through the processes of photosynthesis and respiration. Biotic production and decomposition affect the pH in line with the equation (Anderson, 1985; Fraga and Perez, 1990; Fraga *et al.*, 1998)



The vertical profiles of pH on a total scale at 25°C are shown in Figure 2b. The pH reaches a maximum in surface waters ( $8.035 \pm 0.005$ ) due to photosynthesis. The pH then decreases due to the oxidation of plant material and exhibits a sharp decrease with depth to approximately 1000 m coincident with a minimum in  $\text{O}_2$  and maximum in apparent oxygen utilisation (AOU) (Llinás *et al.*, 1999) and  $f\text{CO}_2$ . The lowest values of pH at around 800-900 m (open circles in Fig. 2) trace the northward advection of AAIW (Willenbrink, 1982) as a poleward undercurrent of the Canary Current. On the other hand, the highest  $\text{pH}_t$  values observed between 800-1000 m (from 7.75 to 7.82) are due to the presence of a Meddy (open triangles) around station 871. Below 1000 m, an increase in pH is observed due to the dissolution of calcium carbonate and the advection of water masses more ventilated than the intermediate water masses.

The vertical profiles of total alkalinity show a minimum at around 700 m ( $2335 \mu\text{mol kg}^{-1}$ ), a local alkalinity maximum at 1000 m associated with the Meddy at station 871 ( $2393 \mu\text{mol kg}^{-1}$ ), and increasing alkalinity with depth below 1300 m, (Fig. 2c), following the same pattern as the salinity distribution. When the alkalinity is normalized to a constant salinity of 35 ( $\text{NA}_T = A_T/S \cdot 35$ ) in order to remove the saline effect over  $A_T$  (Fig. 2e), a typical nutrient profile is obtained, with a surface depletion due to formation of calcium carbonate and regeneration at depth due to the temperature and pressure effect on the solution equilibrium of calcium carbonate.

Figures 2d and 2f show the distribution of computed  $C_T$  and  $\text{NC}_T$  ( $\text{NC}_T = C_T/S \cdot 35$ ) in the water column for the most representative stations sampled during the Poseidon 212/3 cruise. The maximum values of  $C_T$  were found in the deepest and less saline waters, NADW, and in the saline core of Mediterranean water (open triangles). The redissolution of calcium carbonate and remineralisation of organic matter is responsible for the increase of  $C_T$  in NADW, whereas the high values of  $C_T$  in MW are due to the saline contribution. The  $C_T$  concentration decreases towards the surface layer due to the uptake of the same by the phytoplankton. Thus, the MW shows a clear signal by its low  $\text{NC}_T$  ( $2117 \mu\text{mol kg}^{-1}$ ), high  $A_T$  ( $2393 \mu\text{mol kg}^{-1}$ ) and relatively high pH. In the strait between Gran Canaria and Fuerteventura (stations 863-865, open circles in Fig.

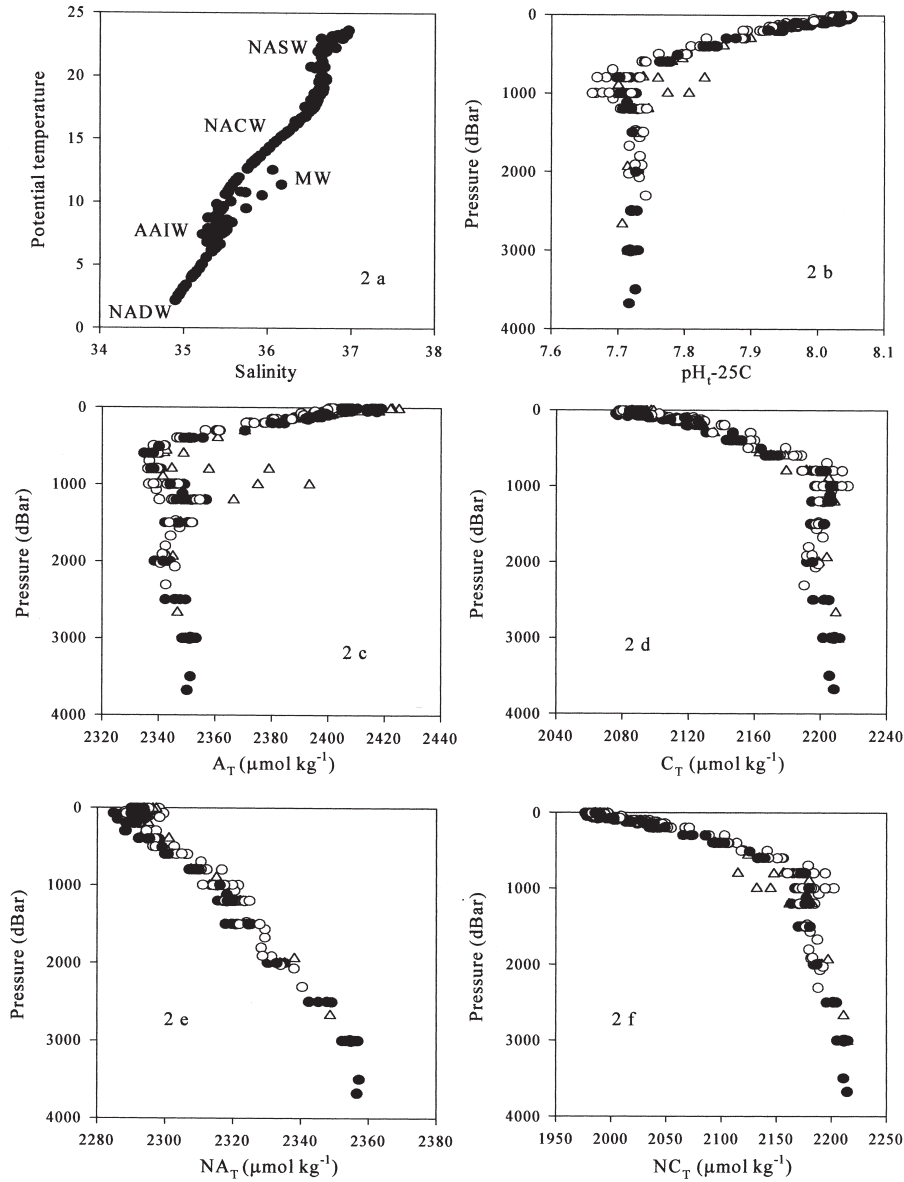


FIG. 2. – Potential temperature-salinity plot (a),  $\text{pH}_{T-25^{\circ}\text{C}}$  profile (b), total alkalinity ( $\mu\text{mol kg}^{-1}$ ) profiles (c), computed total inorganic carbon  $C_T$  ( $\mu\text{mol kg}^{-1}$ ) profiles (d), normalised ( $S = 35$ ) total alkalinity ( $\text{NA}_T$ ) (e) and normalised ( $S = 35$ ) total inorganic carbon  $\text{NC}_T$  profiles (f) over selected stations. Open circles correspond to stations 863-867 and 842-846 in the eastern part, closed circles correspond to ESTOC station (stations 840, 853 and 869) and open triangles to stations 870 and 874 in the western part.

2) the influence of AAIW is shown by its low pH value (7.641), low  $A_T$  ( $2331.3 \mu\text{mol kg}^{-1}$ ) and high  $C_T$  ( $2205.3 \mu\text{mol kg}^{-1}$ ) (high  $C_T$  to  $A_T$  ratio). Below the MW core and the poleward intrusion of AAIW, there is a relatively homogenous layer in pH in comparison with the immediately higher layer.

### Alkalinity and $f\text{CO}_2$ sections

The water mass characteristics observed during the Poseidon 212/3 cruise can be considered typical for the beginning of autumn: high temperature

at the surface and a well-developed thermocline. Figure 3 shows the alkalinity variability over the La Palma-La Graciosa section. The presence of North-Atlantic Central Water (NACW) from 150 to 750 m shows a strong gradient of alkalinity. In the intermediate water from 750 to 1500 m the influence of both Mediterranean Water (MW) and Antarctic Intermediate Water (AAIW) is clearly observed. The influence of AAIW has been found by Rios *et al.* (1992) at  $24^{\circ}\text{N}$  and  $22^{\circ}\text{W}$  with minimum salinity ( $S < 35.4$ ). The minimum salinity in the AAIW corresponds a layer of minimum pH

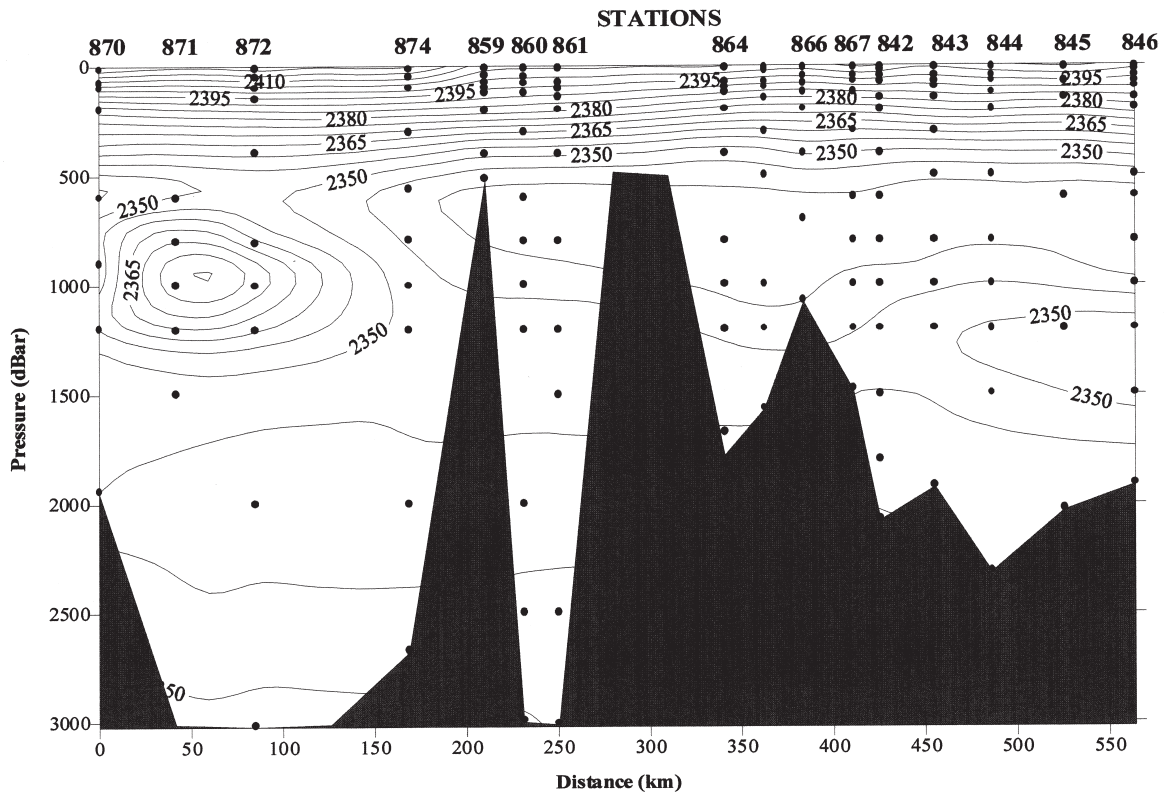


FIG. 3. – Distribution of total alkalinity  $A_T$  ( $\mu\text{mol kg}^{-1}$ ) for La Palma (Station 870) - La Graciosa (Station 846), to the north of the Canary Islands in October 1995. Hereafter the bottom represents the depth observed at each station and is not a typical bathymetric profile.

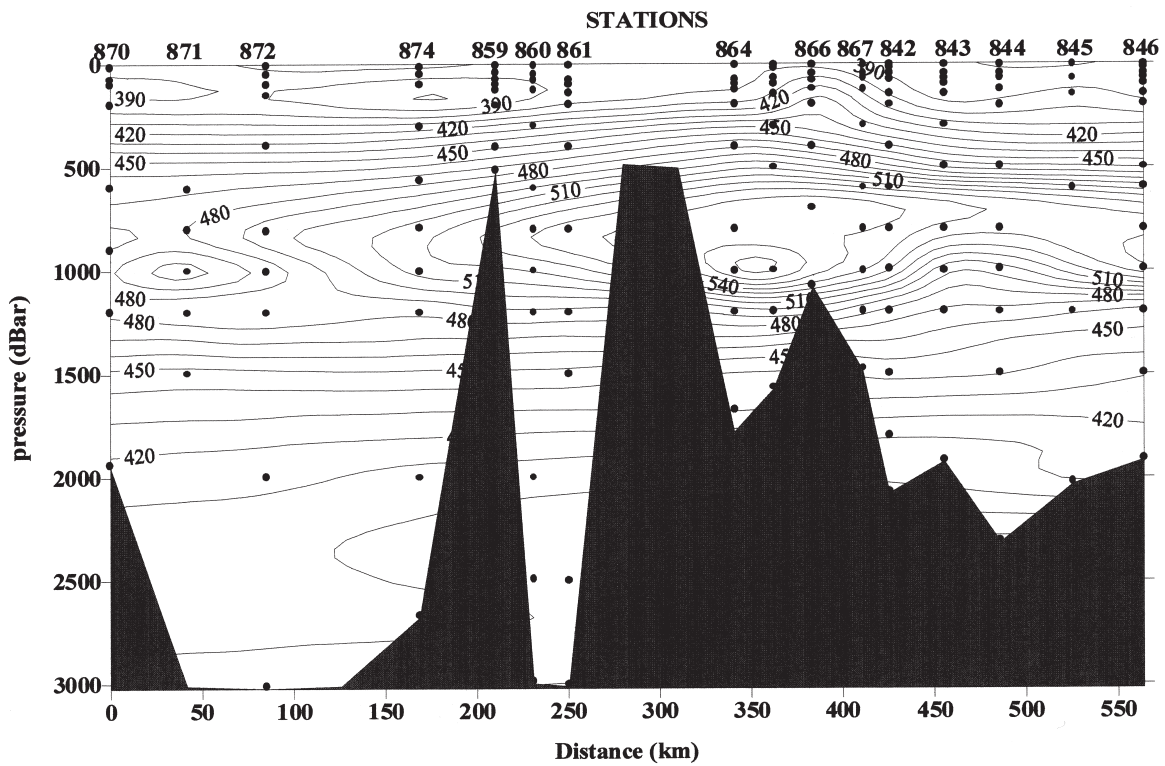


FIG. 4. – The distribution of computed carbon dioxide fugacity ( $\mu\text{atm}$ ) from La Palma (Station 870) - La Graciosa (Station 846), to the north of the Canary Islands in October 1995.

(Fig. 2b), minimum alkalinity (Fig. 3) and maximum  $f\text{CO}_2$  (592  $\mu\text{atm}$ ) (Fig. 4) between stations 864 and 866, which correspond with the inflow of AAIW through the strait between Gran Canaria and Fuerteventura. This maximum fugacity is also observed at station 846 (La Graciosa). This northern salinity minimum is the result of the northward and eastward advection of AAIW within the Gulf Stream-North Atlantic Current system (Measures *et al.*, 1995). The influence of AAIW in this area has also been traced by minimum values of oxygen and slightly higher nutrient concentrations (mainly silicate) by Llinás *et al.* (1999). The maximum salinity at around 1200 m with high values of alkalinity and total dissolved inorganic carbon is due to Mediterranean water (Fig. 2d). At station 871, a high maximum salinity denotes the presence of a Meddy. This Meddy also shows a relative maximum of pH (Fig. 2b) and a sharp increase in alkalinity (Figs. 2c and 3).

The surface values of computed  $f\text{CO}_2$  for this time of the year clearly show that this area is acting as a source of  $\text{CO}_2$ . Assuming a mean atmospheric value of  $f\text{CO}_2$  of 360  $\mu\text{atm}$  and surface values of 385 to 400  $\mu\text{atm}$ , we found that during this cruise this oceanic area tends to release  $\text{CO}_2$  into the atmosphere. The air-sea  $\text{CO}_2$  exchange ( $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) is calculated using the following equation

$$F\text{CO}_2 = 0.24 \cdot k \cdot S \cdot (f\text{CO}_{2,\text{sw}} - f\text{CO}_{2,\text{air}}) \quad (2)$$

where  $k$  is the liquid phase gas transfer velocity ( $\text{cm}\cdot\text{h}^{-1}$ ) and  $S$  is the  $\text{CO}_2$  seawater solubility ( $\text{mol}\cdot\text{kg}^{-1}\cdot\text{atm}^{-1}$ ) (Weiss 1974). The effect of wind speed on the transfer velocity,  $k$ , is obtained from the equation (Wanninkhof, 1992)

$$k = (0.31 * U_{10}^2) \cdot (660/Sc)^{1/2} \quad (3)$$

$U_{10}$  is the wind speed at a height of 10 m ( $\text{m s}^{-1}$ ). The averaged wind speed during this cruise was  $10 \pm 3 \text{ m s}^{-1}$ . The Schmidt number,  $Sc$ , is determined from a third-order polynomial fit for the temperature dependence (Wanninkhof, 1992).

The resulting air-sea  $\text{CO}_2$  flux was  $+8.0 \pm 1.8 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ . Considering the observed variability of  $f\text{CO}_2$  in this area in 1996-1997 (González-Dávila *et al.*, 2000), this positive  $\text{CO}_2$  flux can be considered as a maximum value on an annual scale. However, on the same scale this value is clearly compensated, showing this area as a slight sink of  $\text{CO}_2$  (Takahashi *et al.*, 1997)

## State of saturation

The precipitation or formation of solid  $\text{CaCO}_3$  in surface waters and the dissolution of solid  $\text{CaCO}_3$  in deep water is very important in transferring  $\text{CO}_2$  from surface waters to deep waters. A close coupling of seasonal phytoplankton maxima and particle flux peaks at the ESTOC station has been found (Neuer *et al.*, 1994). This characteristic of many areas of the Atlantic has been demonstrated in the Sargasso Sea by Deuer *et al.* (1990) and in the North Atlantic Bloom Experiment (NABE, 47°N, 20°W) by Newton *et al.* (1994). It was mediated by rapid transfer of surface water production to deep ocean. The saturation state of seawater with respect to a carbonate phase ( $\Omega_i$ ) can be determined by calculating the ratio of the measured total ion concentration product to the apparent solubility product of carbonate  $i$  ( $K_{\text{sp},i}$ ) according to Equation 4. The thermodynamic index of the apparent solubility product from which the degree of saturation is calculated depends on  $f\text{CO}_2$  and pH, pressure,  $T$  and mineralogy (aragonite or calcite).

$$\Omega_i = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp},i}^* \quad (4)$$

The surface waters in this area are well supersaturated with respect to both calcite and aragonite. The surface value of  $\Omega$  for calcite is  $5.6 \pm 0.2$  and  $3.6 \pm 0.2$  for aragonite, both of which decrease in deep water. Aragonite from pteropods is more soluble than calcite from foraminifera and coccolithophorids at a given  $T$ ,  $p$  and  $S$ . During this cruise total coccolithophore cell densities showed a strong gradient from open ocean localization (station 870) with 18.000 cell  $\text{l}^{-1}$  to the near-shore location (near the African coast) with 45.000 cell  $\text{l}^{-1}$ . Maximum cell densities occurred in the upper photic zone above the deep chlorophyll maximum, which was located between the depth of 50 m and 125 m (Knoll *et al.*, 1998).

The saturation level for aragonite is 2700 m and for calcite is higher than 3500 m. The greater solubility of these minerals in deep waters relates to the effect of pressure on the solubility of  $\text{CaCO}_{3(s)}$ .

## Inorganic and organic derived carbon

The processes related to the deep dissolution of  $\text{CaCO}_3$  and decomposition of organic carbon provide a direct mechanism for the renewal of carbon and related elements in the sea and are of funda-

mental interest in the biogeochemical cycles of these elements. Studying the nature of the particulate matter in traps in this area, Fischer *et al.* (1996) found that coccolithophorids (coccoliths and coccospheres) constitute a dominant part of the particulate matter. The close correlation of organic carbon and carbonate sedimentation at 1000 m and 3000 m trap depths founded by Neuer *et al.* (1997) confirms the important role of coccolithophorids as primary producers and in the export flux in the Canary Island region during all seasons. These authors found a considerable increase in particle flux with depth, probably caused by the interaction of fast sinking particles originating from a primary source region close to the area with those advected laterally from closer to the NW African upwelling margin.

To calculate the quantity of calcium carbonate that has dissolved in the water column, the change in salinity normalised  $A_T$  and  $C_T$  values must be determined. It must be considered that the water masses present in this area may have had different  $A_T$  and  $C_T$  values at the time when the water masses were formed. Therefore, to calculate properly the  $\Delta NA_T$  and  $\Delta NC_T$  values, the preformed values ( $NA_T^\circ$  and  $NC_T^\circ$ ) must be determined. Given the preformed values in a body of water and its present values, it is possible to determine the ratio of in situ inorganic and organic carbon decomposition. Under the assumption that  $A_T$  is not affected by the

invasion of anthropogenic  $CO_2$ , we do not have to differentiate between historical and contemporary  $NA_T^\circ$  values. However, the  $NC_T^\circ$  values must be corrected for the injection of anthropogenic  $CO_2$ . Failure to correct the  $NC_T^\circ$  values for anthropogenic  $CO_2$  may result in an error of 0.05-0.07 in the inorganic carbon to organic carbon ratio (Chen, 1990). The estimated amount of excess  $CO_2$  in this area is  $\approx 62 \mu\text{mol/kg}$  (Körtzinger *et al.*, 1998). Several authors (Edmon, 1974; Chen and Pytkowicz, 1979; Körtzinger *et al.*, 1998) have reported linear correlation between the potential temperature  $\theta$  and salinity normalized values of surface  $A_T$  and  $C_T$ . The linear regressions calculated from our data set (this cruise and unpublished data,  $n = 42$ ) in order to calculate the preformed values for the deep waters in this area are given by

$$NA_T^\circ = 2294.3 (\pm 3.4) - 0.27 (\pm 0.17) \theta \quad (5)$$

$$NC_T^\circ = 2183.7 (\pm 6.2) - 10.02 (\pm 0.80) \theta \quad (6)$$

Using Equations 5 and 6, the ratio of carbon contributed to the waters from inorganic sources (IC) to carbon derived from the decomposition of organic matter (OC) can be calculated from Equations 7 to 9 (Chen *et al.*, 1982; 1987; Chen, 1990)

$$\Delta NA_T = NA_{T(\text{measured})} - NA_T^\circ \quad (7)$$

$$\Delta NC_T = (NC_{T(\text{measured})} - NC_T^\circ) + 62 \quad (8)$$

$$IC/OC = (0.15094 \Delta NC_T + \Delta NA_T) / (2 \Delta NC_T - \Delta NA_T) \quad (9)$$

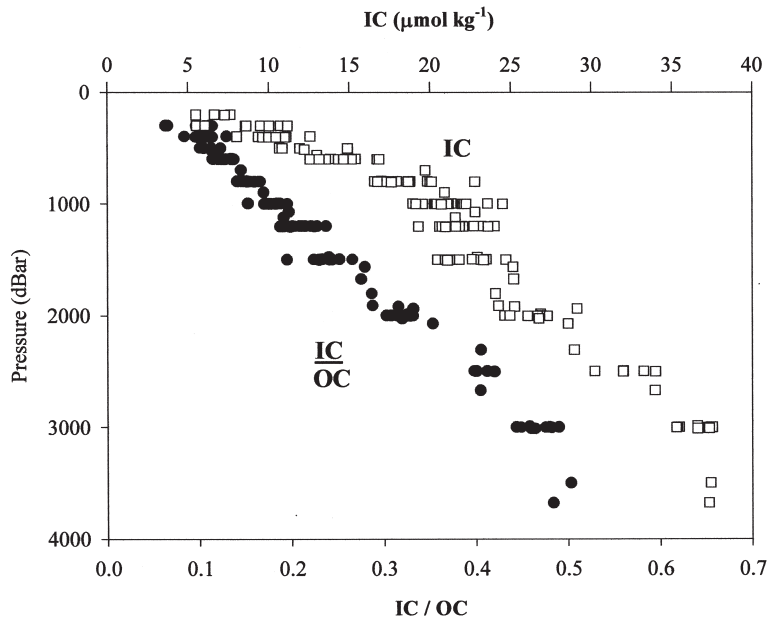


FIG. 5. – Ratio of carbon derived from the dissolution of calcium carbonate (IC) to carbon derived from the decomposition of organic matter (OC) calculated from Equations 7 to 9 (closed circles) and inorganic carbon in the water column contributed by the dissolution of carbonate particles, IC, determined from Equation 10 (open squares) over the water column.

The IC/OC was calculated for waters deeper than 300 m and is shown in Figure 5. The IC/OC ratio increases from 0.07 at 300 m to 0.5 at 3000 m. These values are higher than the ratio of 0.17 found in the Sea of Japan (Chen *et al.*, 1995) and 0.36 found in the North Pacific (Chen, 1990), and similar to the value of 0.52 found in the Bering Sea (Chen, 1993). An IC/OC value of 0.5 indicates that approximately 34% of the carbon in the deep Canary area is contributed by the dissolution of carbonate particles. It should be pointed out that an error of 15% in the amount of excess CO<sub>2</sub> in this area only contributes in an error of 2% in the IC/OC ratio. Our results demonstrate that far more carbon is added to the deep ocean from the decomposition of organic matter than from the dissolution of carbonates. Neuer *et al.* (1997) obtained that the flux of organic carbon explained more than 70% of the variability of the sedimentation of carbonate and lithogenic material. The increase in IC/OC with depth indicates that carbonate dissolution increases as a function of depth relative to the rate of decomposition. This is consistent with saturation state calculations, which demonstrate that deep waters are more undersaturated with respect to carbonate than shallow waters.

The quantity of inorganic carbon in the water column contributed by the dissolution of carbonate particles may be calculated from Equation 10 considering IC + OC = ΔNC<sub>T</sub> (Sabine *et al.*, 1995)

$$IC = 0.07018 \Delta NC_T + 0.4649 \Delta NA_T \quad (10)$$

The IC at 300 m is approximately 7 μmol kg<sup>-1</sup>, increasing with depth to 37.5 μmol kg<sup>-1</sup> at 3700 m. Again, an error of 15% in the amount of excess CO<sub>2</sub> in this area only contributes in an error of less than 1 μmol kg<sup>-1</sup> in the IC. The increase in IC demonstrates that the dissolution of carbonate particles (aragonite and calcite) increases with depth as they sink through the water column. This increase in IC must therefore be primarily due to the dissolution of aragonite particles.

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