

## The CO<sub>2</sub> system in the Mediterranean Sea

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# The CO<sub>2</sub> system in the Mediterranean Sea: a basin wide perspective

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## Abstract

This paper provides an extensive vertical and longitudinal description of the CO<sub>2</sub> system variables (Total Alkalinity – TA, dissolved inorganic carbon – DIC and pH) along an East-West transect and across the Sardinia–Sicily passage in the Mediterranean Sea (MedSea) from two oceanographic cruises conducted in 2011 measuring CO<sub>2</sub> variables in a coordinated fashion, the RV *Meteor* M84/3 and the RV *Urania* EuroFleets 11, respectively.

The over-determined CO<sub>2</sub> system allowed performing the first internal consistency analysis for the particularly warm, high salinity and alkalinity MedSea waters. This basin is considered a “laboratory basin” suffering dramatic changes in its oceanographic and biogeochemical conditions derived from natural and anthropogenic forces. Despite this, little is known about the CO<sub>2</sub> system variability in the whole basin. This work aims to be a benchmark for future studies about the CO<sub>2</sub> system space-time variability in the MedSea. In this sense we provide full-depth and length CO<sub>2</sub> distributions across the MedSea, and property – property plots showing in each sub-basin post-Eastern Mediterranean Transient (EMT) situation with regard to TA, DIC and pH.

## 1 Introduction

The Mediterranean Sea (MedSea hereafter) is a particular system with respect to its physical and biogeochemical oceanography (e.g., Tanhua et al., 2013a). The Med-Sea is a land-locked sea exporting warm and salty intermediate water into the Atlantic Ocean through the shallow and narrow Strait of Gibraltar affecting the global thermohaline circulation. Apart from the shallow open thermohaline cell encompassing the whole Mediterranean basin, two closed deep overturning cells are active in the western and eastern basins, respectively. Additionally, a complex upper layer circulation is present including significant permanent and quasi-permanent eddies.

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One of the most relevant biogeochemical characteristics of the MedSea, especially the eastern basin, is the anomalous high Nitrogen to Phosphorous ratio (e.g. Ribera d'Alcalà et al., 2003; Krom et al., 2005; Pujo-Pay et al., 2011). This fact along with the oligotrophic gradient from west to east could be attributed to the difference in the allochthonous nutrient sources in terms of quantity and quality (Ribera d'Alcalà et al., 2003; Ludwig et al., 2010; Schroeder et al., 2010; Krom et al., 2010) and also to the specific hydrodynamic features of the MedSea (Robinson et al., 2001; Millot and Taupier-Letage, 2005; Huertas et al., 2012).

With a limited exchange with the ocean and its specific circulation, the MedSea is considered a “laboratory basin” (e.g., Robinson and Golnaraghi, 1994; Bergamasco and Malanotte-Rizoli, 2012) where processes occurring on a global scale can be approximated to smaller time and space scales. This fact mostly mentioned for general circulation studies can also be applied for biogeochemical studies, eutrophication, hypoxia, acidification, etc.

The MedSea represents only 0.8% of the global oceanic surface and despite the general sparseness of water column carbon measurements (Álvarez, 2012) it has been identified as an important anthropogenic carbon storage where the column inventory is much higher than in the Atlantic or Pacific oceans (Schneider et al., 2010; Lee et al., 2011). The reasons for this is the intrinsic physico-chemical characteristics of the MedSea where warm and high alkalinity waters, thus low Revelle factor, are prone to absorb CO<sub>2</sub> from the atmosphere and be transported to the interior by the active overturning circulation.

This paper is a contribution to the Special Issue “Physical, chemical and biological oceanography of the Mediterranean Sea”. In particular it focuses on CO<sub>2</sub> system analysis performed on board RV *Meteor* (M84/3 cruise) and RV *Urania* (EuroFleets 11 cruise), both sampled the MedSea in April 2011 (Tanhua et al., 2013a) (Fig. 1). Vertical distributions and property–property plots will be presented and discussed in order to characterize the different MedSea sub-basins with regard to the CO<sub>2</sub> system.

## 2 Data and methods

### 2.1 Meteor M84/3 cruise

During the *Meteor* M84/3 cruise in April 2011 (Fig. 1) (Tanhua et al., 2013a, b) Dissolved Inorganic Carbon (DIC), pH and total alkalinity (TA) were measured in all stations and depths in order to have an over-determined CO<sub>2</sub> system. Details about the sampling, analysis and quality control are given in Tanhua et al. (2013b). The bottle data is available at the Carbon Dioxide Information Analysis Center (CDIAC) (Tanhua et al., 2012).

The DIC content was determined using a SOMMA instrument. Samples were collected in borosilicate bottles according to standard operation protocol. The precision of the analysis was determined to  $\pm 0.6 \mu\text{mol kg}^{-1}$  by titration of several bottles filled from the same Niskin bottle. The accuracy was determined to be  $2.5 \mu\text{mol kg}^{-1}$  by analyzing a total of 42 bottles of certified reference material (CRM, Andrew Dickson, Scripps, CA, USA, batch 108); the DIC of this batch is certified at  $2022.70 \pm 0.7 \mu\text{mol kg}^{-1}$ . Measurements of the CRMs were also used to daily correct the temporal drift in the coulometer cell; this correction was never larger than  $3 \mu\text{mol kg}^{-1}$ .

pH was measured in cylindrical optical glass 10 cm pathlength cells with a spectrophotometric procedure (Clayton and Byrne, 1993). pH is reported in the total scale at 25 °C (pH25T). The precision was estimated to  $\pm 0.0012$  by measuring replicates from the same Niskin bottle. Regarding the accuracy, the theoretical pH25T value for the 108 CRM batch using the dissociation constants from Mehrbach et al. (1973) refitted by Dickson and Millero (1987) is 7.8782. Replicate pH measurements along the cruise on CRMs are lower than the theoretical value by  $0.0962 \pm 0.0012$  pH units. We will discuss this point in Sect. 3.2.

Samples for TA determination were collected in 600 mL borosilicate bottles and were analyzed within one day after sampling. The TA samples were analyzed following the double end point potentiometric technique by Pérez and Fraga (1987) and Pérez et al. (2000). Measurements of CRM were performed in order to control the accuracy

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of the TA measurements; the pH as measured by the electrode was corrected to obtain the closest mean TA to the CRM; the pH correction was never larger than 0.05. The precision of the TA measurements was better than  $0.6 \mu\text{mol kg}^{-1}$  determined from duplicate Niskin bottles, and the accuracy of the TA measurements (i.e. including sampling errors) is determined to be  $1 \mu\text{mol kg}^{-1}$ . Additionally, the daily drift of the system was determined by regular measurements of a substandard (surface seawater); this drift was always very low.

Other data used in this study from the M84/3 cruise are the hydrographic variables from CTD (Continuous Temperature Depth) casts, and the bottle data for dissolved oxygen measured by a Winkler potentiometric technique and inorganic nutrients measured with a Quattro auto-analyzer. See Tanhua et al. (2013b) for more details. The Apparent Oxygen Utilization (AOU) is calculated using the saturation equation from Benson and Krause (1984).

### 2.2 *Urania* EF11 cruise

During the EF11 survey samples for DIC, pH and TA were collected and measured on land. Unfortunately, fewer stations (15 for TA and pH, and 9 for DIC) than originally planned (Tanhua et al., 2013b) were sampled due to the geopolitical situation in the area. Two inter-calibration stations with the M84/3 cruise in the Ionian Sea were occupied (Fig. 1). All samples were carefully sampled in borosilicate glass bottles, poisoned with mercuric chloride, sealed with grease (silicone) and stored in the dark at a constant temperature of about  $12^\circ\text{C}$ , until the analyses in the laboratories on shore (ISMAR for TA and pH and GEOMAR for DIC).

In ISMAR pH was measured as described in the previous section, with the spectrophotometric procedure described by Clayton and Byrne (1993), and reported at  $25^\circ\text{C}$  and on the Total scale. The precision was estimated in  $\pm 0.003$  measuring replicates from the same Niskin bottle. Regarding the accuracy, the theoretical pH<sub>25T</sub> value for the CRM batch 100, using the dissociation constant from Merbach et al. (1973) refitted by Dickson and Millero (1987), is 7.907. Our pH replicates on CRMs batch 100

are lower than the theoretical value by  $0.019 \pm 0.003$  pH units. We further checked the accuracy against Tris Buffer Solution Synthetic Seawater batch 13 (distributed by Dr. Dickson), with certified pH corresponding to 8.093 pH<sub>25T</sub>. Our replicates on Tris are lower than the theoretical value by  $0.018 \pm 0.004$ . As the two different accuracies match very well, this correction was applied to the EF11 pH values.

TA was determined by potentiometric titration in an open cell with a difference derivative readout (Hernandez-Ayon et al., 1999). The precision of the TA measurements was better than  $2.3 \mu\text{mol kg}^{-1}$  determined from duplicate Niskin bottles. The accuracy of the TA measurements on CRM (batch 117) is determined to be  $0.8 \mu\text{mol kg}^{-1}$ , as our results yielded a mean value of  $2240.0 \mu\text{mol kg}^{-1}$ , comparable to the certified value  $2339.2 \mu\text{mol kg}^{-1}$ . The daily drift of the system was determined by regular measurements of substandard seawater; this drift was always very low.

The DIC was analysed at GEOMAR with the same methodology and equipment as in M84/3. Precision and accuracy of measurements are the same as those reported for the M84/3 cruise, see above.

### 3 Consistency of CO<sub>2</sub> analysis

#### 3.1 Inter-cruise consistency

A crossover analysis was performed between the M84/3 and EF11 CO<sub>2</sub> data using the methodology applied to the CARINA database (Tanhua et al., 2010). We studied two areas: the Tyrrhenian Sea (4 stations each cruise) and the Ionian Sea (3 stations from M84/3 and 2 from EF11) (Fig. 1). We compared the DIC, pH and TA data below 1000 dbars: DIC difference is less than  $2 \mu\text{mol kg}^{-1}$  in both sites; EF11 TA is about  $11 \mu\text{mol kg}^{-1}$  higher and was therefore reduced by this amount, and pH<sub>25T</sub> differences are quite noisy and less than 0.01. Therefore, EF11 CO<sub>2</sub> data were not included in the following analysis of the internal consistency of the CO<sub>2</sub> system, Sect. 3.2.

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Using the preferred set of constants reported on in Sect. 3.2 we compared measured DIC with that calculated from pH and TA using option 4 and the CO<sub>2</sub>SYS program for MATLAB (see next section). After rejecting some outliers, the mean difference between measured and calculated DIC is  $-0.4 \pm 10 \mu\text{mol kg}^{-1}$ . In summary, no adjustments were done to the EF11 DIC and pH measurements, whereas the TA was reduced by  $11 \mu\text{mol kg}^{-1}$  as a consequence of the comparison between M84/3 and EF11 data.

The EF11 CO<sub>2</sub> data will be used to discuss the CO<sub>2</sub> system properties in water masses of the passage between Sardinia and Sicily, Sect. 4.1.1.

### 3.2 Internal consistency analysis for the CO<sub>2</sub> system in the MedSea

There is a wealth of literature regarding the internal consistency of CO<sub>2</sub> analysis in seawater and its dissociation constants, see the review by Millero (2007), but to the best of our knowledge the last study about this issue was published in 2002 compiling up to 6000 measurements from NSF/JGOFS, NOAA/OACES and DOE/WOCE cruises in the Atlantic, Pacific, Southern and Indian oceans (Millero et al., 2002), but without any CO<sub>2</sub> data from the MedSea.

Despite lacking of surface or column partial pressure CO<sub>2</sub> ( $p\text{CO}_2$ ) measurements, this study presents high-quality DIC, TA and pH data covering the whole MedSea that can be used to perform the first internal consistency analysis in this area for CO<sub>2</sub> measurements.

By using the consensus program for seawater CO<sub>2</sub> calculations CO<sub>2</sub>SYS, configured for Matlab by van Hueven et al. (2011) we tested the internal consistency of our measurements for the various CO<sub>2</sub> constants using all options, except that for pure water only (option 8). We also changed the sulfate constants (Dickson, 1990; Khoo, 1977) and the parameterization of borate as a function of salinity (Uppström, 1979; Lee et al., 2010). The inorganic nutrients concentrations were also taken into account.

The option yielding minimum differences between the calculated and measured variable for the three combinations (TA-pH, TA-DIC and DIC-pH) (Table 1 and Fig. 2) is obtained by using option 4 (CO<sub>2</sub> constants from Mehrbach et al., 1973 refitted by Dick-

son and Millero, 1987), the sulphate constant from Dickson (1990) and the parameterization of borate from Uppström (1979). Using this borate function and the sulphuric constant from Khoo (1977) yields practically the same results (not shown). Using option 13 (Millero et al., 2006), the more recent borate function by Lee et al. (2010) and either sulphate constant (Khoo, 1977 or Dickson, 1990) low residuals are also obtained (not shown).

By using our preferred set of constants (see above) our pH, TA and DIC measurements along the M84/3 cruise are internally consistent to  $-0.0003 \pm 0.005$  for pH,  $0.1 \pm 3.3 \mu\text{mol kg}^{-1}$  for TA and  $-0.1 \pm 3 \mu\text{mol kg}^{-1}$  for DIC. This combination of constants is also the preferred option in global ocean  $\text{CO}_2$  data synthesis projects such as GLODAP (Key et al., 2004) and CARINA (Key et al., 2010). At the light of these results, the bias of  $0.0962 \pm 0.0012$  in the pH25T measurements obtained after CRM measurements for pH during M84/3 was disregarded.

The effect of uncertainties in  $pK_1$  and  $pK_2$  using the pH–TA combination is identical to those observed using pH–DIC. As summarized in Lee et al. (1997) when pH and TA (pH and DIC) are used as input parameters, calculated DIC (TA) depends on  $pK_2$ , which is also dependent upon the DIC/TA ratio; the lower the ratio the higher the sensitivity to  $pK_2$ . However, only a reliable  $pK_1$  is needed to calculate  $p\text{CO}_2$  from the pH–TA (pH–DIC) combination; in this case the lower the DIC/TA ratio the lower the sensitivity to  $pK_1$ . Calculated pH from the TA–DIC input combination relies on a good estimation of  $pK_1 - pK_2$  (the  $K_1/K_2$  ratio). The DIC/TA ratio is an indicative of the concentration of carbonates; the lower the ratio the higher the  $[\text{CO}_3]^{2-}$  concentration, which is also sensitive to  $pK_2$ . Lacking measured  $p\text{CO}_2$  data we are not able to check the dependence on  $K_1$  in the calculation of  $p\text{CO}_2$  (pH–DIC or pH–TA inputs) or pH ( $p\text{CO}_2$ –DIC or  $p\text{CO}_2$ –TA inputs).

Having the former information in mind, a closer look at the pH, TA and DIC residuals (measured minus calculated values) reveals some insights and peculiarities about the internal consistency of  $\text{CO}_2$  measurements in the high TA (low DIC/TA) and salinity MedSea waters. Figure 3 shows the longitudinal distribution of the residuals in the

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MedSea pointing to a decreasing trend eastwards for TA (Fig. 3a) and on the contrary an increasing trend eastwards for DIC and pH (Fig. 3b and c) which seem to be related with the eastwards salinity increase (Fig. 3 in Tanhua et al., 2013a), DIC/TA ratio decrease (Fig. 10h) or  $[\text{CO}_3]^{2-}$  increase. The pH residuals are a function of  $pK_1 - pK_2$ , but mostly dependent on  $K_2$ , while the TA or DIC residuals are a function of  $pK_2$  (Lee et al., 1997; Millero, 2007). The relation between pH and TA residuals is linear (Fig. 4) but two regression lines are detected depending on salinity. Samples with salinity higher than 36.1 have a higher slope ( $-0.0015 \pm 4.5 \times 10^{-6}$ ,  $r^2 = 0.9937$ ,  $n = 725$ ) than fresher ones ( $-0.0020 \pm 2.9 \times 10^{-5}$ ,  $r^2 = 0.9945$ ,  $n = 28$ ). Including measured pH, TA and DIC data from five CARINA cruises (Key et al., 2010) between the Strait of Gibraltar and  $24^\circ \text{W}$  and  $40^\circ \text{N}$  to  $24^\circ \text{N}$  the same tendency is detected (data with salinity  $< 36.1$ , slope =  $-0.0022 \pm 8.7 \times 10^{-6}$ ,  $r^2 = 0.9919$ ,  $n = 671$ ; data with salinity  $\geq 36.1$ , slope =  $-0.0016 \pm 6.7 \times 10^{-6}$ ,  $r^2 = 0.9977$ ,  $n = 182$ ). This result points to the need for a revision of the  $K_2$  parameterization for waters with high salinity and low DIC/TA ratio, as in the MedSea, as the CO<sub>2</sub> chemistry is more sensitive to  $K_2$ .

In summary, the preferred option for CO<sub>2</sub> constants for global studies on internal consistency (CO<sub>2</sub> constants from Mehrbach et al., 1973 refitted by Dickson and Millero, 1987; sulphate constant from Dickson, 1990; total borate from Uppström, 1979) also applies for MedSea waters. However, further studies are needed, with an additional fourth measurement, either  $p\text{CO}_2$  or  $[\text{CO}_3]^{2-}$  (Byrne and Yao, 2008) to confirm the internal consistency of  $K_1$  and  $K_2$  with the measurements in the peculiar MedSea waters.

#### 4 Distribution of CO<sub>2</sub> species in the Mediterranean Sea

The general aim of this section is to provide, for the first time, a large-scale distribution of measured and derived CO<sub>2</sub> properties along the full length of the Mediterranean Sea and corresponding sub-basins, being complementary to the physical (temperature and salinity) and chemical (dissolved oxygen and inorganic nutrients) variables presented

by Tanhua et al. (2013a). Water mass characterization will be commented using vertical distributions and property–property plots for the different sub-basins.

## 4.1 Vertical distributions

### 4.1.1 Measured variables

#### 5 *Meteor M84/3* cruise data

Vertical distributions of TA (Fig. 5), DIC (Fig. 6) and pH25T (Fig. 7) clearly distinguish several water masses in the MedSea, from surface to bottom:

(i) Levantine Surface Water (LSW): this water formed by intensive heating and evaporation, has the largest salinity and temperature of the entire MedSea ( $> 17^{\circ}\text{C}$ ,  $> 38.9$ ), clearly seen in the surface layer of the Levantine Basin (Tanhua et al., 2013a). LSW presents TA values around  $2610\ \mu\text{mol kg}^{-1}$ , DIC around  $2270\ \mu\text{mol kg}^{-1}$  and pH25T around 8.03 (Figs. 5–7).

(ii) Atlantic Water (AW): enters through the Strait of Gibraltar and flows eastward, it is mainly detected by a low salinity signal in the upper 50–100 dbars (Fig. 3 in Tanhua et al., 2013a) from the Strait of Gibraltar to the Levantine Basin (36.2–38.9). AW also presents a low TA signal evolving from values  $< 2560\ \mu\text{mol kg}^{-1}$  in the western basin to higher ones in the Levantine Basin and Ionian Sea ( $< 2600\ \mu\text{mol kg}^{-1}$ ) (Fig. 5). The same trend was seen in DIC evolving from  $2250\ \mu\text{mol kg}^{-1}$  in the western to  $2270\ \mu\text{mol kg}^{-1}$  in the Levantine Basin (Fig. 6). But the opposite was found for pH25T, which increases from 8 to 8.014 (Fig. 7).

The MedSea is considered one of the most oligotrophic areas in the world (Azov, 1991) with low phytoplankton biomass and primary production decreasing eastward, confirmed by in situ measurements (Ignatiades et al., 2009; Moutin and Raimbalut, 2002; Siokou-Frangou et al., 2010), satellite data (Bosc et al., 2004; Volpe et al., 2007; D’Ortenzio and Ribera d’Alcalà, 2009) and modelling studies (Crise et al., 1999, 2001; Lazzari et al., 2012). Oligotrophy originates from the low concentration and supply

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of nutrients into surface waters during most of the year; this is intensified when the water column is thermally stratified during spring and late fall. Surface Chlorophyll *a* (Chl *a*) and primary production data during the M84/3 cruise are presented in Rahav et al. (2013) with a clear westward increasing gradient, and values ranging from 0 to 0.4  $\mu\text{g L}^{-1}$  for Chl *a*, and 0.2 to 15  $\mu\text{g C L}^{-1} \text{d}^{-1}$  for primary production. The period of the M84/3 cruise, April coincides with the end of the winter-spring bloom (D'Ortenzio and Ribera d'Alcalà, 2009; Lazzari et al., 2012).

The gathered biogeochemical data during the M84/3 cruise shows that the upper 50 dbars are supersaturated in oxygen (AOU < 0) with more negative values in the western basin pointing to higher primary production as confirmed by direct measurements (Rahav et al., 2013). While in the western basin inorganic nutrients are still available, in the eastern basin they are depleted, especially phosphate (see corresponding figures in Tanhua et al., 2013a). For waters with Pres < 60 dbars, there is no clear relationship between AOU and either DIC, TA or pH<sub>25T</sub>, except in the western basin where pH<sub>25T</sub> relates with AOU ( $\text{pH}_{25T} = -0.0015 \pm 0.00008 \times \text{AOU} + 7.97 \pm 0.001$ ,  $r^2 = 0.83$ ,  $p < 0.001$ ), pointing to a modulation of pH by primary production.

(iii) Levantine Intermediate Water (LIW): this warm and high salinity water is formed in the Levantine Basin, mainly in the Rhodes Gyre area. During the M84/3 cruise LIW was clearly detected by the salinity maximum around 200 dbars in the eastern basin (Tanhua et al., 2013a), with TA > 2620  $\mu\text{mol kg}^{-1}$ , DIC > 2310  $\mu\text{mol kg}^{-1}$  but no clear signal in pH which varies between 7.96 and 7.98 (Figs. 5–7). In the western basin LIW was found around 500 dbars as a maximum in salinity, corresponding to TA ( $\approx 2590 \mu\text{mol kg}^{-1}$ ) (Fig. 5), maximum in DIC ( $\approx 2330 \mu\text{mol kg}^{-1}$ ) (Fig. 6) and minimum pH<sub>25T</sub> ( $\approx 7.9$ ) (Fig. 7). In the eastern basin, the maximum layer of remineralization indicated by the oxygen minimum (see Fig. 6 in Tanhua et al., 2013a) is located below LIW while in the western basin, both coincide.

(iv) Eastern Mediterranean Deep Water (EMDW): along the M84/3 cruise track in the eastern MedSea two types of EMDW can be distinguished mainly using salinity (Fig. 3 in Tanhua et al., 2013a) and tracers as CFC-12 (Stöven and Tanhua, 2013). In the

Levantine Basin below 1500 dbars the water column was occupied by a more saline (Tanhua et al., 2013a) water than in deep layers of the Ionian basin. In the Ionian Sea, recent EMDW was characterized by higher DIC (Fig. 6, lower panel) values by about  $5 \mu\text{molkg}^{-1}$  compared to EMDW in the Levantine Basin, but no such a clear signal was detected either in TA or pH25T (Figs. 5–7). In the Levantine Basin the deep water has an Aegean Sea origin produced during the EMT (Eastern Mediterranean Transient) event while in the Ionian Sea EMDW has a more recent Adriatic Sea component produced after the EMT (Hainbucher et al., 2013).

The upper panels in Figs. 5, 6 and 7 show the distribution of  $\text{CO}_2$  species in the through the centre of the Ionian Sea to the Adriatic Pit. In this section, below 3000 dbars DIC (Fig. 6) increased towards the bottom, a feature not seen neither in salinity or TA (Fig. 5). A slight, but hard to detect, decrease in pH25T (Fig. 7) was also noted. The tracers distributions, CFC-12 and  $\text{SF}_6$  (Stöven, 2012), also increase towards the bottom. These results point to a recent addition of EMDW formed in the Adriatic Sea. In the centre of the Ionian Sea the broad pH minimum between 125 and 1000 dbars extends trough LIW and the upper part of EMDW, also covering the layer of maximum remineralization centred at 1000 dbars as indicated by the oxygen minimum (Tanhua et al., 2013a).

(v) Western Mediterranean Deep Water (WMDW): being fresher and colder than EMDW, the deep layers below 1500 dbars in the western MedSea during M84/3 were quite homogeneous in the physical (potential temperature and salinity) properties but a closer look showed two distinct WMDW, a younger one as noted by the CFC-12 distribution (Stöven, 2012) and saltier than the WMDW immediately above 2000 dbars (Hainbucher et al., 2013). Bottom (younger) WMDW also presented higher DIC values by about  $7 \mu\text{molkg}^{-1}$ , lower pH25T values by about 0.004, and higher TA values by about  $4 \mu\text{molkg}^{-1}$ , i.e., within the accuracy limits of the latter two variables (Figs. 5–7).

Another outstanding feature in the vertical distribution of  $\text{CO}_2$  variables was the pH25T minimum (Fig. 7) around 500 dbars in the Levantine and Ionian basins. In the Levantine basin this minimum was coincident with the oxygen minimum (Fig. 6 in Tan-

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hua et al., 2013a) and a DIC maximum (Fig. 6). Whereas in the Ionian Sea the pH25T minimum/DIC maximum (500 dbars) was shallower than the oxygen minimum that was situated around 1000 dbars. All these extreme layers were not coincident with LIW, the salinity maximum was shallower in both basins, Levantine and Ionian. However, in the western basin, the LIW signal was coincident with the layer of highest remineralization as indicated by the DIC maxima and the oxygen/pH25T minimum.

During the M84/3 cruise we sampled the interior of the Tyrrhenian Sea: in the upper layer low salinity (Tanhua et al., 2013a) and TA values (Fig. 5) point to AW. Around 400 dbars the maximum in salinity, TA, DIC and pH25T (Figs. 5–7) are associated with LIW entering through the Sicily channel; Tyrrhenian Deep Water (TDW) formed from the mixing of LIW and WMDW was detected below the TA maximum associated with LIW and bottom water with lower TA and pH25T and higher DIC values (Figs. 5–7). This bottom water corresponds to WMDW that has started to cascade into the Tyrrhenian Sea from the western basin in 2011, also higher in tracer concentrations (Stöven and Tanhua, 2013).

As a reference for future studies and calculations in Sect. 4.1.2, Table 2 shows the mean and standard deviation values for salinity and different CO<sub>2</sub> species in the Med-Sea sub-basins and Atlantic waters west of the Strait of Gibraltar as sampled in 2011 during the *Meteor* M84/3 cruise by different depth intervals.

The direct comparison of our CO<sub>2</sub> data with previously published CO<sub>2</sub> data, either DIC, TA or pH, in order to detect trends and variability is out of the scope of our manuscript. We do however make a rough comparison in order to detect possible biases in the historic data set as compared to ours and vice versa. Qualitatively, our TA and DIC data in the western MedSea seems to be 5–10 and 40–70  $\mu\text{mol kg}^{-1}$  lower, respectively, than those shown in Millero et al. (1979) from a cruise in 1976. This result is counterintuitive due to the expected increase in DIC due to input of anthropogenic carbon ( $C_{\text{ANT}}$ ). However, the data from Millero et al., (1979) originates from before the use of certified reference materials (CRMs), so that the accuracy of these early data can be questioned. Our TA and DIC are however more comparable to those from the Almofront

cruise in 1991 (Copin-Montegut, 1993). The data shown by Touratier and Goyet (2009) from the DYFAMED site in the Ligurian Sea below 1000 dbar, corresponding to WMDW, are lower than our WMDW values by about  $5 \mu\text{mol kg}^{-1}$  for both DIC and TA.

The reference cruise for the carbonate system in the eastern MedSea is the M51/2 cruise (RV *Meteor* 2001); the TA data was presented in Schneider et al. (2007) and the DIC in Schneider et al. (2010). The TA data are comparable but our DIC are roughly  $10 \mu\text{mol kg}^{-1}$  higher, which could be a real signal considering the 10 yr between the measurements and the uptake of anthropogenic carbon.

The VECTOR cruise in 2007 sampled 8 stations in the eastern and western Med-Sea for pH and TA, whereas DIC was calculated (Rivaro et al., 2010). Examining data from the western basin below 700 dbars, the TA data are comparable to each other whereas the DIC and pH values reported by Rivaro et al. (2010) are higher than ours by  $10 \mu\text{mol kg}^{-1}$  and by 0.01, respectively. In the eastern basin, our data below 700 dbars for pH and TA are comparable but our DIC seems  $20 \mu\text{mol kg}^{-1}$  higher. More recent  $\text{CO}_2$  data are reported from the BOUM cruise in 2008 (Pujo-Pay et al., 2011); their DIC data seem higher than ours by about  $10 \mu\text{mol kg}^{-1}$  in both the eastern and western basins.

## Sardinia Sicily Passage

The vertical distributions of physical properties in the Sardinia Sicily passage, already analysed in the last decade of last century (Astraldi et al., 2002), indicate that the passage is a crucial chokepoint where almost all MedSea waters can be intercepted (see a review of the general characteristics of the transect in Fig. 5 of Astraldi et al., 2002). This section focuses on the description of the oceanographic settings in the Sardinia Sicily passage as sampled during the *Urania* EF11 cruise. The Sardinia Sicily transect, for its local character, was not included in the overall MedSea description done by Tanhua et al. (2013a). The main water masses crossing the passage have been identified according to their physical characteristics using potential temperature and salinity (Fig. 8a and b), AOU, (Fig. 8c) and  $\text{CO}_2$  variables (Fig. 8d–f). On the eastern part (close to Sicily) only inflowing waters can be observed, from surface to bottom: (1)

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A fresh vein of AW (0–200 dbars), coming directly from Gibraltar through the Algerian sub-basin, is evident from the low salinity ( $\ll 38.00$ ) (Fig. 8b) and supported by the lowest TA values ( $2525\text{--}2575\ \mu\text{mol kg}^{-1}$ ) (Fig. 8d); this inflowing AW is not in equilibrium with atmospheric oxygen (AOU between  $20\text{--}40\ \mu\text{mol kg}^{-1}$ , Fig. 8c), pH<sub>25T</sub> ( $\approx 7.950$ , Fig. 8f) and DIC values ( $2225\text{--}2285\ \mu\text{mol kg}^{-1}$ , Fig. 8e) are the lowest observed along the section. (2) Below AW, the inflow of the saltiest water ( $> 38.75$ ) in the transect, LIW, coming from the eastern MedSea, after crossing the Sicily Channel, the high AOU ( $50\text{--}60\ \mu\text{mol kg}^{-1}$ ) and DIC ( $\approx 2300\ \mu\text{mol kg}^{-1}$ ) values aside of the low pH<sub>25T</sub> ( $< 7.940$ ) highlight the organic matter remineralization processes occurring within the LIW; TA values as high as  $2605\text{--}2610\ \mu\text{mol kg}^{-1}$  were observed. (3) Below LIW, there is thin layer (not always distinctly present) of dense transitional Eastern Mediterranean Deep Water (tEMDW, i.e. the upper layer of the deep water filling the Eastern Mediterranean, which is able to cross the channel); tEMDW is cooler and fresher than LIW ( $< 13.8\ ^\circ\text{C}$  and  $< 38.65$ ), as well as for the higher DIC, TA ( $2318$  and  $2612\ \mu\text{mol kg}^{-1}$ , respectively, Fig. 8d, e) and inorganic nutrient values (not shown) and the lower pH<sub>25T</sub> ( $< 7.930$ , Fig. 8f); given its high density tEMDW cascades at greater depths to the interior of the Tyrrhenian Sea, contributing to the formation of the Tyrrhenian Deep Water, TDW, and provoking an intense mixing that dilutes its original physical properties (tEMDW is significantly warmer and saltier than TDW), in contrast the chemical properties of these two deep water masses remain very similar (Fig. 8).

On the western part (close to Sardinia) there are both inflowing and outflowing water masses, from surface to bottom: (1) close to Sardinia the outflowing AW has circulated through the Tyrrhenian Sea, becoming saltier ( $38.00 < \text{salinity} < 38.20$ , note the depth decrease towards Sardinia of the 38 isoline, Fig. 8b) and even less saturated in oxygen (AOU  $35\text{--}40\ \mu\text{mol kg}^{-1}$ , note the depth decrease towards Sardinia of the 20 isoline, Fig. 8c) than the inflowing AW on the Sicilian side; CO<sub>2</sub> variables are also slightly different ( $2550 < \text{TA} < 2575\ \mu\text{mol kg}^{-1}$ ;  $2270 < \text{DIC} < 2285\ \mu\text{mol kg}^{-1}$ ;  $7.940 < \text{pH}_{25T} < 7.950$ , note the sloping isolines in Fig. 8d–f). (2) Below the outflowing AW, an outflowing LIW vein can be noted, which in turn, after its path through

the whole Tyrrhenian Sea has become colder ( $\approx 14.0^\circ\text{C}$ ) and less salty ( $< 38.68$ ) than the inflowing LIW on the eastern edge of the section, due to the mixing; this fact also lowers TA ( $\approx 2600\ \mu\text{mol kg}^{-1}$ , Fig. 8d) and increases DIC ( $\approx 2310\ \mu\text{mol kg}^{-1}$ , Fig. 8e) while the pH25T (Fig. 8f) remains similar; outflowing LIW is also characterized by an absolute AOU maximum ( $65 < \text{AOU} < 73\ \mu\text{mol kg}^{-1}$ , Fig. 8c) due to ageing. (3) In the central part of passage, over the plateaux, there is an inflow of “old LIW” (Astraldi et al., 2002) (identified by its salinity maximum, but less salty than the outflowing LIW), also identified by higher AOU ( $55\text{--}70\ \mu\text{mol kg}^{-1}$ , Fig. 8c) than the inflowing LIW ( $50\text{--}60\ \mu\text{mol kg}^{-1}$ ), while differences in  $\text{CO}_2$  variables cannot be distinguished. (4) In deep layers ( $600\text{--}1900$  dbars) the properties of LIW progressively become those of TDW, exiting the Tyrrhenian Sea, pH25T show the lowest values ( $< 7.930$  Fig. 8f), AOU and DIC the highest ones ( $72 < \text{AOU} < 74\ \mu\text{mol kg}^{-1}$ ;  $2315 < \text{DIC} < 2320\ \mu\text{mol kg}^{-1}$ , Fig. 8c and e) and TA values ( $> 2605\ \mu\text{mol kg}^{-1}$ , Fig. 8d) are not particularly characterizing. (5) At the bottom and squeezed on the eastern wall in the deep canyon, there is an inflowing vein of Western Mediterranean Deep Water, which can be distinguished from the TDW because is fresher ( $< 38.52$ ) and colder ( $< 13.4^\circ\text{C}$ ), has slightly lower AOU ( $< 70\ \mu\text{mol kg}^{-1}$ ), higher pH25T values ( $> 7.940$ ) but similar DIC ( $> 2318\ \mu\text{mol kg}^{-1}$ ) and TA ( $2605\text{--}2610\ \mu\text{mol kg}^{-1}$ ) values.

#### 4.1.2 Derived variables

We used measured TA, DIC and inorganic nutrients data to calculate the degree of saturation ( $\Omega$ ) for calcite and aragonite using the MATLAB version for CO2SYS with the preferred set of constants (see Sect. 3.2). The whole MedSea is supersaturated ( $\Omega \gg 1$ ) with respect to both calcite and aragonite throughout the whole water column. Figure 9 shows the vertical distribution of  $\Omega$ , a clear longitudinal gradient is evident for surface, intermediate and deep waters with increasing values eastwards and a clear separation between the western, eastern MedSea basins and Atlantic waters to the west of the Strait of Gibraltar. The  $\Omega$  values reported here compare well with those found by Millero et al. (1979) and Schneider et al. (2007). According to the classifica-

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tion by Kleypas et al. (1999) only the eastern basin in the upper 200 dbars presents adequate to optimal conditions for the development of coral reefs with  $\Omega\text{-Ar} > 3.5$ .

This work expects to be a benchmark for future studies predicting the effects of acidification in the MedSea from the chemical and biological point of view. Several projects, finished (e.g., EPOCA) or on going (e.g., BIOACID, MedSea), try to decipher the combined effect of acidification and warming on the highly adapted MedSea calcareous and non-calcareous organisms. Because of being too small but too complex in its circulation and biogeochemistry the MedSea is usually not included in global projections models (e.g., Ricke et al., 2013) and a specific ocean-biogeochemistry model needs to be used. Here we provide a basin wide perspective for the  $\text{CO}_2$  chemistry in the MedSea as a basis for future studies and projections.

In order to quantify the ability of MedSea waters to resist changes in the  $\text{CO}_2$  system we calculated the buffer factors formulated by Egleston et al. (2010). The six factors proposed in their Table 1 quantify the sensitivity of aqueous  $\text{CO}_2$  [ $\text{CO}_2$ ] ( $\gamma_i$ ), protons [ $\text{H}^+$ ] ( $\beta_i$ ) and the carbonate saturation state  $\Omega$  ( $\omega_i$ ) to changes in DIC and TA (subindex  $i$ ) when the other parameter is kept constant. The calculations were performed with the output from  $\text{CO}_2\text{SYS}$  at in situ conditions with the preferred set of constants and measured DIC and TA as inputs. The buffer factors have dimensions of  $\text{mol kg}^{-1} \times 10^{-3}$  of seawater ( $\text{mmol kg}^{-1}$  hereinafter). See the formulation in Table 3 as several editing errors were detected in the original equations from Egleston et al. (2010).

The buffer factors  $\gamma_i$  express the fractional change in  $\text{CO}_2$  when DIC changes at constant TA (air-sea  $\text{CO}_2$  exchange) or when TA changes at constant DIC (additions of strong acid or base). The traditional Revelle factor,  $R$ , is directly calculated as  $R = \text{DIC}/\gamma_{\text{DIC}}$ . The buffer factor  $\beta_{\text{TA}}$  expresses the fractional change in hydrogen ion concentration or activity when TA changes at constant DIC (addition of a strong base or acid). The factor  $\beta_{\text{DIC}}$  is identical to  $-\gamma_{\text{TA}}$ . Since  $[\text{Ca}^{2+}]$  and the solubility products of carbonate are invariant to DIC and TA changes, the buffer factors  $\omega_i$  account for the fractional change in  $[\text{CO}_3^{2-}]$  when DIC or TA changes when correspondingly TA

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or DIC is constant. A natural process just inducing strong acid/base additions is difficult to imagine, but a cargo disaster could be possible, unfortunately. A change in a natural process (primary production/remineralization of organic matter, formation/dissolution of carbonates, freshwater balance) usually affects both TA and DIC and therefore, the sensitivity of [CO<sub>2</sub>], pH and [CO<sub>3</sub><sup>2-</sup>] to a change in those processes can be calculated using a combination of buffer factors (Egleston et al., 2010).

The values of  $\gamma_{\text{DIC}}$  and  $\beta_{\text{DIC}}$  are positive while  $\omega_{\text{DIC}}$  is negative because adding CO<sub>2</sub> to seawater increases [CO<sub>2</sub>] and [H<sup>+</sup>] but decreases [CO<sub>3</sub><sup>2-</sup>]. Likewise,  $\gamma_{\text{TA}}$  and  $\beta_{\text{TA}}$  are negative while  $\omega_{\text{TA}}$  is positive because adding a strong base to seawater decreases [CO<sub>2</sub>] and [H<sup>+</sup>] but increases [CO<sub>3</sub><sup>2-</sup>]. Low buffer values imply low buffering capacity for a given change in DIC or TA. Minimum absolute values for the six buffer factors are found in waters with similar DIC and TA (DIC/TA ratio  $\approx$  1) and pH of about 7.5.

The six buffer factors,  $R$  and the DIC/TA ratio are shown in Fig. 10 and their mean values by sub-basin in Table 3. As the DIC/TA ratio approaches one the buffer capacities are reduced since [CO<sub>2</sub>] is more sensitive to temperature changes at this DIC/TA ratio. MedSea waters in the eastern basin have lower DIC/TA ratios than in the western basin (Fig. 10h) and in general, MedSea waters present lower DIC/TA ratios compared to Atlantic waters. The highest ratios, i.e. higher [CO<sub>2</sub>] sensitivity to temperature, for the M84/3 cruise were reported west of the Strait of Gibraltar and associated with the Mediterranean Overflow, DIC/TA ratio  $>$  0.9 (Fig. 10h).

From the vertical distributions in Fig. 10 we can conclude that:

- MedSea water is generally more resistant to changes in DIC and/or TA than Atlantic waters to the west of the Strait of Gibraltar, since all buffer factors are lower in the Atlantic.
- The CO<sub>2</sub> system in the western basin is in general more sensitive to changes in DIC and/or TA than the eastern basin, i.e., buffer factors are lower in the western basin.

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– The absolute buffering capacities distribute as  $|\omega_{DIC}| > \omega_{TA} > |\beta_{TA}| > (\beta_{DIC} = -\gamma_{TA}) > \gamma_{DIC}$ . That is, the sensitivity of CO<sub>2</sub> concentration to changes in DIC at constant TA (air–sea CO<sub>2</sub> exchange) is the highest, followed by the change in pH due to the air–sea CO<sub>2</sub> exchange (equivalent to the change in CO<sub>2</sub> due to a strong acid/base addition), then changes in pH due to strong acid/base additions. Being  $|\omega_{DIC}|$  and  $\omega_{TA}$  the highest buffer values means that MedSea waters are able to buffer more easily than Atlantic waters changes in the saturation state due to additions of a strong acid or base and the air–sea CO<sub>2</sub> exchange.

– By examining the Revelle factor it is obvious that for a given change in CO<sub>2</sub> the relative change in DIC for MedSea waters is higher than in the adjacent Atlantic waters. That means that MedSea waters have the ability to store more anthropogenic carbon (C<sub>ANT</sub>) than Atlantic waters. Within the MedSea the eastern basin is more prone to absorb more C<sub>ANT</sub> for a given CO<sub>2</sub> increase than the western basin.

The impact of the three main anthropogenic processes altering the surface CO<sub>2</sub> chemistry in MedSea waters is given in Table 4, which shows absolute changes in aqueous CO<sub>2</sub> ([CO<sub>2</sub>]), pH and the aragonite saturation ( $\Omega$ –Ar) from the initial surface values in Table 2; the different sub-basins are treated separately. A C<sub>ANT</sub> input through air–sea exchange (affecting DIC at constant TA) increasing DIC by 10  $\mu\text{mol kg}^{-1}$  will lead to an increase of [CO<sub>2</sub>] from 0.56 to 0.78  $\mu\text{mol kg}^{-1}$ , a pH decrease of around 0.016 units in MedSea waters, less than the pH decrease in Atlantic waters (0.020) for the same perturbation; the saturation state is reduced by about 0.1 units, but a reduction of at least 0.9 is required for deep waters to become under-saturated in aragonite. A hypothetical decrease in calcification, resulting in a DIC increase of 10  $\mu\text{mol kg}^{-1}$  and double in TA, will compensate the pH and  $\Omega$  decrease due to the input of C<sub>ANT</sub> and roughly half the corresponding increase in [CO<sub>2</sub>]. Within the MedSea changes in [CO<sub>2</sub>] and pH increase westwards being smaller than in Atlantic waters. An increase in salinity of 0.03 will cause minor changes in the CO<sub>2</sub> chemistry.

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The buffer factors here provided are useful to predict changes in the CO<sub>2</sub> chemistry as a function of DIC and/or TA changes due to different processes, natural and/or anthropogenic. However, it is relevant to relate the increase of C<sub>ANT</sub> in the ocean to the increasing partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>) in the atmosphere instead of using a DIC increase as reference. Table 5 shows the absolute changes in DIC, pH and Ω–Ar from initial states in Table 2 as a consequence of prescribed *p*CO<sub>2</sub> increases. Note that a *p*CO<sub>2</sub> increase of 25 μatm causes changes in DIC by about 10 μmol kg<sup>-1</sup>, as already presented in Table 4. The main result in Table 5 is that as the Revelle factor in warm, salty and high TA waters is lower (Table 3) the change in DIC for a given *p*CO<sub>2</sub> increase is higher and consequently the changes in Ω–Ar and pH. Therefore, MedSea waters are more sensitive to DIC changes induced from the *p*CO<sub>2</sub> increase in the atmosphere (C<sub>ANT</sub> increase) despite having higher buffer factors.

### 4.2 Water mass characterization

Up to our knowledge no work has presented the chemical characterization with regard to CO<sub>2</sub> variables for water masses in the western and eastern MedSea sub-basins. Here we present property–property plots for general physical and chemical variables, typical potential temperature–salinity, AOU–salinity and silicate concentration (SiO<sub>2</sub>)–salinity (Figs. 11 and 13) and the CO<sub>2</sub> variables, TA, DIC and pH<sub>25T</sub> vs. salinity, SiO<sub>2</sub> and AOU (Figs. 22 and 14). We separated the western and eastern basins showing with colours the different sub-basins comprised. Some special characteristics, mainly in deep waters, are presented in more detail with figures in the Supplement. The companion paper by Hainbucher et al. (2013) gives a wider description of the physical and hydrodynamical variability.

#### (a) Aegean Sea (stations 287, 288 and 289):

The Aegean Sea was early recognized as a source of dense waters (Nielsen, 1912) but not dense enough to contribute to the EMDW (e.x., Wüst, 1961). This traditional view changed after the EMT event was detected (Roether et al., 1996).

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During this period high amounts of warm and saline CDW (Cretan Deep Water) denser than Adriatic EMDW filled the deep layer south of the Cretan Straits, lifting the previous EMDW to shallower depths.

Three stations during the M84/3 cruise were located in the Aegean Sea: 287 in the Chios Basin (central Aegean Sea), 289 in the eastern Cretan basin and 289 in the Kasos Strait (both in the southern Aegean Sea). In the upper 100 dbars high salinity identifies LSW (Levantine Surface Water) entering the Aegean Sea through the eastern Cretan arc straits (Fig. 11a). This LSW is also identified by the highest pH<sub>25T</sub> values measured in the M84/3 cruise (> 8.01, Fig. 12h) and also high TA and DIC values (≈ 2620 and ≈ 2280 μmol kg<sup>-1</sup>, respectively, Fig. 12a and d). At intermediate levels, 100 to 250 dbars, CIW (Cretan Intermediate Water) presents the highest TA values for the M84/3 cruise (≈ 2645 μmol kg<sup>-1</sup>, Fig. 12a and d). Deep layers below 2500 dbars are occupied by CDW (Cretan Deep Water), warm, salty and very dense (Fig. 11a) (Hainbucher et al., 2013), identified by the distinct SiO<sub>2</sub>–salinity relation (Fig. 11c), practically constant DIC (≈ 2320 μmol kg<sup>-1</sup>) and TA (≈ 2630 μmol kg<sup>-1</sup>) values vs. SiO<sub>2</sub> (Fig. 12b and e).

(b) *Levantine Basin* (from station 290 to 298):

In the upper water column, < 100 dbars, AW and LSW can be distinguished using salinity (Fig. 11a), LSW presents salinity > 38.9 and less variable values than AW with salinity ranging from 38.58 to 38.9 decreasing westwards (Fig. 11a and Fig. 3 in Tanhua et al., 2013a). TA, DIC and pH<sub>25T</sub> values much higher in LSW can also differentiate them (Fig. 12a, d and g). Interestingly, LSW presents pH<sub>25T</sub> values higher, and AW lower than 8.01 for waters with AOU < 0 (Fig. 12i).

At intermediate depths, 100–400 dbars, the main water mass is LIW (Levantine Intermediate Water), which is formed by open-sea convection in the northern part of the Levantine Basin. The companion paper by Hainbucher et al. (2013) describes the LIW evolution in the whole MedSea using the M84/3 data. In addition to the typical scorpion tail relation between salinity and potential temperature, LIW is

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recognized by minima of SiO<sub>2</sub> associated with a salinity maximum (Fig. 11c) and high TA ( $\approx 2630 \mu\text{mol kg}^{-1}$ , Fig. 12a) values.

In the deep layers below 1000 dbars within the Levantine basin, the salinity minimum and then a pronounced temperature–salinity inversion (temperature and salinity increase) typically detected during the EMT (Roether et al., 2007) is still detected in this basin (Hainbucher et al., 2013) (red lines in Fig. S1). Water in the inversion is EMDW with an Aegean Sea origin (Aeg-EMDW) produced during the EMT. Below this inversion, temperature and salinity decrease in the stations west of the East Mediterranean Ridge, so deep waters from the Ionian with a lower Aegean signature. Please see the corresponding temperature–salinity diagrams in Hainbucher et al. (2013).

Adriatic EMDW to the west of the East Mediterranean Ridge is differentiated from Aeg-EMDW mainly with AOU and SiO<sub>2</sub> (Fig. 11b and c), both being lower in the Adriatic EMDW, which also contains higher transient tracer values (Stöven and Tanhua, 2013), indicating a more recent origin. It is difficult to separate them using TA, DIC and pH<sub>25T</sub>, both EMDW present similar values, Adriatic EMDW is slightly higher in DIC (around  $5 \mu\text{mol kg}^{-1}$ ) and TA (around  $4 \mu\text{mol kg}^{-1}$ ) and lower in pH<sub>25T</sub> (0.005 pH units) than Aeg-EMDW (Fig. 12c, f and i) (blue and black lines in Fig. S1).

The salinity minimum around 1000 dbars and below the temperature–salinity inversion previously commented provoke a sort of hook in the relationship between DIC–TA–pH<sub>25T</sub> vs. AOU or SiO<sub>2</sub> (red lines in Fig. S1) for deep waters in this basin. DIC and TA decrease with decreasing SiO<sub>2</sub> or AOU until their corresponding maxima (salinity minimum) and then towards the bottom DIC and TA increase with decreasing AOU (increasing salinity). pH is the opposite, it decreases with AOU increasing until the AOU maximum (salinity minimum) and then pH increases and AOU decreases (Fig. S1).

(c) *Ionian Sea* (from station 299 to 309, 314 and 315):

Two upper water masses can be differentiated in the Ionian Sea, AW ( $< 17^{\circ}\text{C}$ ,  $< 38.9$ ) and LSW ( $> 16^{\circ}\text{C}$ ,  $> 38.8$ ) (Fig. 11a). During M84/3 LSW in the Ionian Sea was found in the stations to the western part of the Hellenic Trench (Sts. 299, 300, 301) (Fig. 1). Below the surface waters, two intermediate water masses, LIW and CIW can be distinguished. LIW with temperature and salinity maxima around 200 dbars is also associated with a TA and DIC maximum (Fig. 12a and d). The mixing between LIW and AW produces an exponential relationship between TA and DIC vs. salinity (Fig. 12a and d). Deviations from this relationship towards lower TA and DIC values correspond to LSW in this basin. The other intermediate water detected, CIW, mixes with LIW south of Crete, in the eastern basin was found in stations 299, 300 and 301 to the west of the Antikithera strait. This water mass with also very high salinity, presents an even higher TA than LIW (Fig. 12a–c). For example in the case of the TA vs.  $\text{SiO}_2$  plot (Fig. 12b) CIW is detected as a deviation towards higher values from the typical TA– $\text{SiO}_2$  relationship. CIW is also seen as a hump between 0 to  $30 \mu\text{mol kg}^{-1}$  AOU over the LIW data (Fig. 12c).

Towards the bottom (please see the corresponding zoomed temperature–salinity plots in Hainbucher et al., 2013), the EMT temperature–salinity inversion is eroded in the Ionian Sea. Post-EMT EMDW occupies the layer below 1500 dbars, it presents lower AOU and  $\text{SiO}_2$  values than EMT Aeg-EMDW (Fig. 11b and c) in the Levantine basin. The recent replenishment from the Adriatic Sea, 2001 onwards, is detected as a temperature–salinity increase in bottom waters of the central Ionian Sea (Rubino and Hainbucher, 2007) (green and cyan lines in Fig. S2). These younger bottom waters in the Ionian Sea explain the DIC increase (Fig. 6), AOU and pH25T (Fig. 7) decrease towards the bottom of the Ionian Sea (compare red line with the blue and cyan lines in Fig. S2).

The hook structure in the relationships DIC–TA–pH vs. AOU for deep waters in the Levantine basin (Fig. S1) is here eroded as is the temperature–salinity inversion associated with Aeg-EMDW. The AOU maximum in the Ionian Sea is no longer

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as clearly associated with the salinity minimum as in the Levantine basin. Below 500 dbars DIC and TA decrease with increasing AOU, from the AOU maximum TA practically stays constant and DIC increases. The very recent input of bottom Ad-EMDW is noticed in the pH vs. AOU relationship, from 500 dbars pH decreases with AOU increasing, from the AOU maximum pH increases (AOU decreases) but close to the bottom both pH and AOU decrease (Fig. S2).

(d) *Adriatic Sea* (stations 310 and 313):

No CO<sub>2</sub> data was taken in the western part of the Otranto Strait (Station 311). Therefore only two stations were sampled in the Adriatic Sea for CO<sub>2</sub> variables, one in the Adriatic Pit (313) and one to the east of the Otranto Strait (310). One of the densest deep waters during the M84/3 cruise was sampled in the Adriatic Pit at 1100 dbars (Fig. 13a), but this water remains confined as the Otranto Strait is only 800 m deep (Hainbucher et al., 2013). Waters in the Adriatic present high TA values despite a moderate salinity (Fig. 12a), they are out of the general linear relationship between TA and salinity due to the high TA of the rivers discharging in the area (Luchetta et al., 2010; Cantoni et al., 2012; Copin-Montegut, 1993). The relationship TA vs. SiO<sub>2</sub> is also different for Adriatic waters (Fig. 12b), being lower than the general trend in the eastern MedSea. Additionally DIC and pH in the Adriatic have a distinct signal, high values for DIC and low values for pH in waters with salinity lower than 38.7 (Fig. 12d and g).

The current overflow from the Adriatic stands out in the pH–AOU plot (Figs. 14i and 7 upper panel): pH data for AOU values between 40 and 45 μmol kg<sup>-1</sup> in stations 309 and 310 located in the Otranto Strait, deviate towards 7.94 pH<sub>25T</sub> values, corresponding to waters around 500 dbars in the Adriatic Pit.

(e) *Tyrrhenian Sea* (from station 316 to 321):

This basin acts as a connector between the eastern and the western MedSea, here intermediate waters entering from the east mix with deep waters entering from the west (e.g., Hopkins, 1988; Astraldi et al., 1996). This fact is noticed in

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the property–property plots shown in Fig. 13 were the points corresponding to the Tyrrhenian Sea clearly connect the western and eastern MedSea waters.

In the surface layer, AW with salinity lower than 38 is detected in all the Tyrrhenian stations except 319 in the centre of the basin (Fig. 13a). The freshest AW is seen in station 316, the nearest to Sicily, here AW comes directly from Gibraltar through the Algerian sub-basin. AW is also distinguished by low AOU and SiO<sub>2</sub> values close to zero (Fig. 13b and c). The minimum TA and DIC associated with AW are 2466 and 2178  $\mu\text{mol kg}^{-1}$ , respectively (Fig. 14a and d). In the centre of the Tyrrhenian Sea the upper 52 dbars are occupied by probably modified AW with 38.5 > salinity > 38 affected by evaporation or mixed with the salty intermediate water entering through the Strait of Sicily. This water also presents a different relationship between salinity and pH25T compared to unmixed AW (Fig. 14g).

Maxima salinity values in the intermediate layer between 250 and 500 dbars point to LIW entering from the eastern basin (Fig. 13a). As LIW flows into the Tyrrhenian Sea remineralization processes increase its AOU, DIC and lower pH25T, with extreme values found in St. 319 (cyan line in Fig. S3) in the interior of this basin and at St. 321 (magenta line in Fig. S3) in the Sardinia Channel where aged LIW flows out of the Tyrrhenian Sea into the western basin.

At St. 316 (red line in Fig. S3), the nearest one to Sicily in the Sardinia Sicily passage, the intermediate layer is occupied by a fresher LIW (38.66–38.68) with higher AOU and DIC (lower pH25T and TA) values. It might be LIW mixed with AW returning to the western basin although this is an area where LIW is supposed to enter the Tyrrhenian Sea.

Deep layers in the Tyrrhenian are occupied by TDW with a typical linear relationship in the temperature–salinity plot (Fig. 13a). No hook in the temperature–salinity diagram to lower salinities is detected in bottom waters of the Tyrrhenian Sea, this hook would show the input of recently formed WMDW as detected in the bottom of the western basin (Hainbucher et al., 2013). The WMDW detected in

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the Tyrrhenian is older, lower in CFC12 (Stöven and Tanhua, 2013), than WMDW found in the bottom of the western basin. In the Tyrrhenian Sea bottom WMDW stands out from TDW by the sharp decrease in AOU and pH25T (Fig. 7) and increase in DIC (Fig. 6) for example with salinity (red dots in Fig. S4).

(f) *Western basin* (from station 322 to 336):

The upper layer in this basin is occupied by AW very fresh ( $\ll 38$ ) and practically 100 % saturated in oxygen ( $\text{AOU} \approx 0 \mu\text{mol kg}^{-1}$ ) and with no  $\text{SiO}_2$  (Fig. 13b and c). In the intermediate layer the salinity maximum associated with LIW evolves from 38.67 at St. 322 to 38.51 at St. 336. There is a marked reduction in salinity (and TA) when LIW enters the western basin passing from 38.71 at St. 321 in the Sardinia Channel, 38.67 at St. 322 (right west of the channel) and then 38.51 at St. 323 in the western basin. The change in the other chemical variables,  $\text{SiO}_2$ , AOU, DIC or pH25T is less acute. LIW mixes above with AW and below with WMDW.

When in the western basin, LIW is associated with a maximum in AOU (Fig. 13b), DIC (Fig. 14d) and minimum in pH25T (Fig. 14g), so it is the layer of maximum remineralization of organic matter, contrary to the eastern basin where this layer is right below LIW.

The near bottom layer in the western basin is occupied by a recently formed WMDW with higher salinity, so the temperature–salinity plots present a sort of hook structure (Hainbucher et al., 2013). This new WMDW presents higher DIC and lower AOU than the older WMDW (Figs. 14f and S5).

(g) *Atlantic waters* (from station 337 to 344):

Due to the dramatic scale change, Fig. 13 and 14 show only the data up to St. 338 (corresponding to the Strait of Gibraltar). All the samples collected to the west of this Strait are shown in Fig. S6.

At the Strait of Gibraltar (St. 337 and 338) the intermediate LIW outflowing presents a salinity of 38.48 ( $\text{TA} \approx 2584 \mu\text{mol kg}^{-1}$ ,  $\text{DIC} \approx 2331 \mu\text{mol kg}^{-1}$ ,  $\text{pH25T} \approx$

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7.89, AOU  $\approx 75.3 \mu\text{mol kg}^{-1}$ ) (Fig. 14 and S6). Only at the stations (342 and 344) close to Portugal (pink lines in Fig. S6) in the continental slope the outflow is detected with a salinity of 36.50 (TA  $\approx 2409 \mu\text{mol kg}^{-1}$ , DIC  $\approx 2193 \mu\text{mol kg}^{-1}$ , pH<sub>25T</sub>  $\approx 7.86$ , AOU  $\approx 58.2 \mu\text{mol kg}^{-1}$ ) while in the centre of the Gulf of Cádiz (339 and 340, black and green lines respectively in Fig. S6) is mixed with the upper low salinity central waters and presents a salinity of 36.20 (TA  $\approx 2392 \mu\text{mol kg}^{-1}$ , DIC  $\approx 2202 \mu\text{mol kg}^{-1}$ , pH<sub>25T</sub>  $\approx 7.79$ , AOU  $\approx 93 \mu\text{mol kg}^{-1}$ ).

## 5 Conclusions

Two coordinated cruises sampled the Mediterranean Sea for CO<sub>2</sub> variables (TA, DIC and pH) in 2011: the RV *Urania* EF11 (Sardinia Sicily passage) and the RV *Meteor* M84/3 (East-West full-length transect).

The over-determined and high-quality CO<sub>2</sub> data collected in the M84/3 cruise allowed performing the first internal consistency analysis for CO<sub>2</sub> data in the peculiar warm, salty and low DIC/TA ratio MedSea waters. Using the MATLAB version for the consensus CO2SYS program the preferred set of constants is option 4 (CO<sub>2</sub> constants from Mehrbach et al., 1973 refitted by Dickson and Millero, 1987) along with the sulphate constant from Dickson (1990) and the parameterization of borate from Uppström (1979). Using this combination our pH, TA and DIC measurements from the M84/3 cruise are internally consistent to  $-0.0003 \pm 0.005$  for pH,  $0.1 \pm 3.3 \mu\text{mol kg}^{-1}$  for TA and  $-0.1 \pm 3 \mu\text{mol kg}^{-1}$  for DIC. Despite this encouraging result further studies are needed including a fourth variable:  $p\text{CO}_2$  in order to verify the internal consistency of  $K_1$  (only a reliable  $K_1$  is needed to calculate  $p\text{CO}_2$  from the input of pH–TA or pH–DIC) and  $[\text{CO}_3^{2-}]$  in order to revise the  $K_2$  parameterization in low DIC/TA ratio waters where the CO<sub>2</sub> system is more sensitive to  $K_2$ . Using the combination of pH–TA–DIC only a reliable  $K_2$  is needed in order to calculate bicarbonate, carbonate and aqueous CO<sub>2</sub> (Park, 1969). Particularly comparing measured (Byrne and Yao, 2008) and calculated  $[\text{CO}_3^{2-}]$  could be helpful to revise  $K_2$ .

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The *Meteor* M84/3 data allowed for the first time a full length and depth description of CO<sub>2</sub> variables in the MedSea. This study aims to be a benchmark for future data and model studies about the likely effects of natural (climate) and human (warming, acidification, etc. . . ) driven changes in the CO<sub>2</sub> species and ancillary variables associated.

Our data provides a picture of the post-EMT physical and biogeochemical distributions in the different MedSea sub-basins.

As a general view, the eastern MedSea presents higher TA (2560–2644 μmol kg<sup>-1</sup>) and pH<sub>25T</sub> (7.935–8.032) and less variable DIC (2247–2331 μmol kg<sup>-1</sup>) than the western basin with TA (2388–2608 μmol kg<sup>-1</sup>), pH<sub>25T</sub> (7.861–7.988) and DIC (2110–2336 μmol kg<sup>-1</sup>). Consequently, the saturation for calcite and aragonite in both basins is well above 1, for the eastern basin Ω–Ca vary 2.5–5.78 and Ω–Ar 1.73–3.80 and for the western basin Ω–Ca 2.73–5.25 and Ω–Ar 1.86–3.44.

The CO<sub>2</sub> chemistry in the warm, salty and high TA waters in the MedSea compared to the Atlantic is in general less sensitive to temperature changes because of the low DIC/TA ratio. Therefore, MedSea waters are more resistant to direct changes in DIC and/or TA due to natural and/or anthropogenic processes, since the calculated buffer factors are higher in MedSea waters, showing an increasing westwards gradient. The CO<sub>2</sub> chemistry in the western basin would be more sensitive than in eastern basin.

However, from the point of view of an increasing *p*CO<sub>2</sub> in the atmosphere, that increases indirectly DIC and keeps TA constant in the ocean, waters in the MedSea have a lower Revelle factor than in the Atlantic, and therefore are able to store more DIC for a given *p*CO<sub>2</sub> increase than in the Atlantic and consequently the changes in the CO<sub>2</sub> chemistry (carbonate saturation, species concentration, pH) would be higher than in the Atlantic.

As a summary the water masses encountered according to depth are:

(i) Levantine Surface Water (LSW): warm and salty (> 38.9) surface water (upper 100 dbars) formed by intensive heating and evaporation in the Levantine basin, found during the M84/3 cruise in this basin and the Aegean and Ionian Seas. LSW is characterised by high TA (≈ 2610 μmol kg<sup>-1</sup>) and DIC (≈ 2270 μmol kg<sup>-1</sup>). In April 2011 LSW

presented pH25T > 8.01 associated with AOU < 0 pointing to active photosynthetic activity.

(ii) Atlantic Water (AW): it is the upper part (< 125 dbars) of the open estuarine cell in the MedSea, enters through the Strait of Gibraltar and flows to the Levantine basin while suffering evaporation and heating. The main CO<sub>2</sub> variable showing the presence of AW is TA, which evolves from very low values in the Strait of Gibraltar ( $\approx 2390 \mu\text{mol kg}^{-1}$ ) to high values ( $\approx 2610 \mu\text{mol kg}^{-1}$ ) in the Levantine basin. Evaporation processes and mixing with the salty Levantine Intermediate Water (LIW) induce a practically linear relation between TA and salinity. Another linear relationship was found between pH25T and AOU for the western MedSea in April 2011 pointing to a biological modulation of pH.

(iii) Levantine Intermediate Water (LIW): main intermediate water mass in the MedSea (125–500 dbars), is the lower part of the open estuarine cell in the MedSea. Typically LIW is identified by a scorpion tail in the temperature–salinity diagram associated with a salinity maximum. The main CO<sub>2</sub> variable identifying LIW in any MedSea sub-basin is an intermediate TA maximum evolving from  $\approx 2620 \mu\text{mol kg}^{-1}$  in the Levantine and Ionian basins to  $\approx 2600 \mu\text{mol kg}^{-1}$  in the Tyrrhenian Sea,  $\approx 2590 \mu\text{mol kg}^{-1}$  in the western basin, and  $\approx 2584 \mu\text{mol kg}^{-1}$  overflowing in the Strait of Gibraltar, and finally  $\approx 2409 \mu\text{mol kg}^{-1}$  in the Mediterranean Water located in the Gulf of Cadiz, that then circulates into the North Atlantic.

In the Levantine and Ionian basins LIW is found shallower ( $\approx 250$  dbars) than in the western basin ( $\approx 450$  dbars). In the eastern MedSea LIW is situated above the layer of maximum organic matter mineralization while in the western MedSea they coincide and therefore is associated with a maximum in DIC and AOU and minimum in pH.

(iv) Cretan Intermediate Water (CIW): formed in the Cretan Sea, this intermediate (250 dbars) water is characterized by even higher TA ( $2630\text{--}2645 \mu\text{mol kg}^{-1}$ ) than LIW and detected in the Aegean Sea and the Ionian Sea west of the Antikithera strait.

(v) Cretan Deep Water (CDW): produced by convection in the Cretan Sea, is clearly identified apart of by the high density, by a distinct relation between SiO<sub>2</sub>–salinity, high

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constant TA ( $2630 \mu\text{mol kg}^{-1}$ ) and DIC ( $2320 \mu\text{mol kg}^{-1}$ ) values with varying  $\text{SiO}_2$  ( $2\text{--}4 \mu\text{mol kg}^{-1}$ ). This water remains confined in the Aegean Sea.

(vi) Pre-EMT Eastern Mediterranean Deep Water (EMDW): this water mass is still detected in the Levantine basin by a salinity minimum around 1000 dbars, it presents a minimum in tracer values as CFC-12 or  $\text{SF}_6$ , but also a minimum in pH because is the layer of organic matter remineralization as also indicated by the maximum in AOU and inorganic nutrients in the Levantine basin. Corresponding to pre-EMT conditions is has an Adriatic Sea origin.

(vii) EMT-EMDW: below the salinity minimum in the Levantine basin temperature and salinity increase producing a hook in the temperature-salinity diagram which is associated with the input of EMDW produced in the Aegean Sea during the EMT. Due to a more recent origin it presents lower AOU, slightly higher DIC and pH values than Pre-EMT EMDW.

(viii) Post EMT-EMDW: bottom layers in the Hellenic Trench (Levantine basin) and deep layers ( $> 1000$  dbars) in the Ionian Sea are occupied by EMDW with an Adriatic origin produced after the EMT. The hook in the temperature-salinity diagram is no longer detected and a less salty Post EMT-EMDW occupies the deep layer in the Ionian Sea. This water is also identified by lower AOU and pH values compared to the saltier EMT-EMDW.

Bottom layers in the Ionian Sea, below about 3000 dbars, are occupied by recent overflow waters produced in the Adriatic Sea after 2001. It presents a clear signature in DIC ( $> 2310 \mu\text{mol kg}^{-1}$ ), AOU ( $< 55 \mu\text{mol kg}^{-1}$ ) and pH ( $< 7.967$ ).

(ix) Waters in the Adriatic Sea: surface waters in this basin present a distinct TA vs. salinity relationship with values around  $2610 \mu\text{mol kg}^{-1}$  for salinity  $< 38.7$ , higher than the general TA-salinity relation mainly due to the high TA input through Adriatic rivers. The overflow from the Adriatic Sea is mainly detected in the pH vs. AOU relationship, for AOU values between  $40\text{--}45 \mu\text{mol kg}^{-1}$  pH deviates to 7.94, those are waters from around 500 dbars in the Adriatic Pit spilling into the Ionian Sea.

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(x) Waters in the Tyrrhenian Sea: the property–property plots shows that this basin is a connector between the eastern and western basins, where LIW mixes deep waters from the west producing Tyrrhenian Deep Water (TDW). During 2011 no recently formed Western Mediterranean Deep Water (WMDW) was detected in the bottom of the Tyrrhenian Sea.

The water mass exchange between the eastern and western MedSea is highlighted using data from the *Urania* EF11 cruise in the Sardinia Sicily passage: AW mainly enters the Tyrrhenian on the eastern part of the passage, close to Sicily, and exits this basin on the Sardinian side, becoming saltier and also higher in TA; the same circulation scheme is done by LIW, which becomes colder and saltier after circulating in the Tyrrhenian, TA is decreased and DIC increased.

(xi) Western Mediterranean Deep Water (WMDW): this water occupies layers below 1000 dbars in the western basin of the MedSea, with respect to CO<sub>2</sub> variables it presents DIC (2318–2320 μmol kg<sup>-1</sup>) higher and TA (2584–2588 μmol kg<sup>-1</sup>) and pH<sub>25T</sub> (7.90–7.91) lower than EMDW. In the bottom layer a recent input, after 2005, of WMDW is detected with higher salinity and temperature, while DIC (AOU) clearly increases (decreases) towards the bottom.

(xii) In the Strait of Gibraltar LIW presents in 2011 a salinity of 38.48 and TA ≈ 2584 μmol kg<sup>-1</sup>, DIC ≈ 2331 μmol kg<sup>-1</sup>, pH<sub>25T</sub> ≈ 7.89, AOU ≈ 75.3 μmol kg<sup>-1</sup>; once mixed with central waters in the Gulf of Cadiz, Mediterranean Water sampled in the Portuguese slope is detected with a salinity of 36.50, TA ≈ 2409 μmol kg<sup>-1</sup>, DIC ≈ 2193 μmol kg<sup>-1</sup>, pH<sub>25T</sub> ≈ 7.86, AOU ≈ 58.2 μmol kg<sup>-1</sup>.

The CO<sub>2</sub> and ancillary data collected in 2011 highlight the need for a sustained program monitoring the temporal evolution of water masses in the MedSea. This small but relevant marginal sea is as a perfect laboratory basin to detect the effect of natural and anthropogenic driven changes in the physics and CO<sub>2</sub> chemistry. Special emphasis should be given to CO<sub>2</sub> variables as MedSea waters are especially sensitive to pCO<sub>2</sub> increases in the atmosphere: they are prone to absorb more DIC for given pCO<sub>2</sub> increase, this DIC increase in the surface is rapidly transported to depth with the over-

turning circulation, and therefore pH and carbonate saturation conditions are altered, with consequences still unknown for the well adapted organisms.

**Supplementary material related to this article is available online at:**  
<http://www.ocean-sci-discuss.net/10/1447/2013/osd-10-1447-2013-supplement.pdf>.

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**Table 1.** Mean and standard deviation of the residuals (measured minus calculated) for alkalinity (TA), Dissolved Inorganic Carbon (DIC) and pH at the total scale and referred to 25 °C (pH25T) calculated with different thermodynamic constants for CO<sub>2</sub> according to the CO2SYS program options. The sulphate constant from Dickson (1990) and total borate concentration from Khoo et al. (1977) were used in all cases.

Constants	TA	DIC	pH25T
1	-16.1 ± 4.0	14.7 ± 3.6	0.024 ± 0.005
2	-11.1 ± 3.7	10.2 ± 3.4	0.016 ± 0.005
3	-5.0 ± 3.5	4.6 ± 3.2	0.007 ± 0.005
4	0.1 ± 3.3	-0.1 ± 3.0	-0.0003 ± 0.005
5	-3.7 ± 3.5	3.4 ± 3.2	0.005 ± 0.005
6	6.3 ± 3.2	-5.9 ± 3.0	-0.009 ± 0.005
7	-3.6 ± 3.5	3.3 ± 3.2	0.005 ± 0.005
9	17.3 ± 3.2	-16.1 ± 3.0	-0.027 ± 0.005
10	0.6 ± 3.3	-0.6 ± 3.0	-0.001 ± 0.005
11	-4.3 ± 3.6	3.9 ± 3.3	0.006 ± 0.005
12	-10.2 ± 4.4	9.3 ± 4.0	0.015 ± 0.006
13	2.8 ± 3.3	-2.6 ± 3.1	-0.004 ± 0.005
14	1.5 ± 3.4	-1.4 ± 3.1	-0.002 ± 0.005

1 – Roy (1993); 2 – Goyet and Poisson (1989); 3 – Hansson (1973a, b) refit by Dickson and Millero (1987); 4 – Mehrbach et al. (1973) refit by Dickson and Millero (1987); 5 – Hansson (1973a, b) and Mehrbach et al. (1973) refit by Dickson and Millero (1987); 6 – GEOSECS choice (Takahashi et al., 1982); 7 – Peng et al. (1987); 9 – Cai and Wang (1998); 10 – Lueker et al. (2000); 11 – Mojica-Prieto and Millero (2002); 12 – Millero et al. (2002); 13 – Millero et al. (2006); 14 – Millero et al. (2010).

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**Table 2.** Mean and standard deviation values for salinity and CO<sub>2</sub> species in the different Med-Sea sub-basins and west of the Strait of Gibraltar as sampled during the M84/3 cruise. Several vertical intervals are considered: surface (0–150 dbars in the East and 0–200 dbars in the West MedSea), intermediate (East: 150–500 and West: 200–500 dbars), deep (East: 500–2500 and West: 600–2000 dbars) and bottom (East: > 2500 and West: > 2000 dbars). IS stands for in situ values. Ar stands for aragonite and Ca for calcite.

	Salinity	TA μmol kg <sup>-1</sup>	DIC μmol kg <sup>-1</sup>	pH25T	CO <sub>2</sub> IS μmol kg <sup>-1</sup>	Ω-Ar IS	Ω-Ca IS
<b>SURFACE</b>							
Aegean	39.20 ± 0.01	2628 ± 2	2291 ± 4	8.009 ± 0.006	13.1 ± 0.2	3.7 ± 0.1	5.6 ± 0.1
Levantine	39.05 ± 0.13	2612 ± 10	2277 ± 15	8.010 ± 0.017	13.1 ± 0.6	3.6 ± 0.1	5.5 ± 0.2
Ionian	38.73 ± 0.21	2607 ± 16	2289 ± 17	7.985 ± 0.015	13.5 ± 0.6	3.4 ± 0.1	5.1 ± 0.2
Adriatic	38.70 ± 0.12	2616 ± 1	2298 ± 16	7.980 ± 0.023	14.0 ± 0.9	3.5 ± 0.2	5.3 ± 0.2
Tyrrhenian	38.32 ± 0.29	2570 ± 26	2294 ± 32	7.929 ± 0.021	16.2 ± 1.0	3.1 ± 0.1	4.7 ± 0.2
Western	37.79 ± 0.51	2522 ± 46	2250 ± 54	7.930 ± 0.033	15.9 ± 1.6	3.0 ± 0.2	4.6 ± 0.2
Atlantic	36.75 ± 0.89	2423 ± 83	2166 ± 83	7.927 ± 0.038	14.6 ± 1.7	2.7 ± 0.2	4.1 ± 0.3
<b>INTERM.</b>							
Aegean	39.14 ± 0.02	2636 ± 2	2318 ± 8	7.975 ± 0.01	14.3 ± 0.4	3.4 ± 0.1	5.1 ± 0.2
Levantine	39.04 ± 0.11	2621 ± 4	2310 ± 10	7.970 ± 0.016	14.6 ± 0.6	3.3 ± 0.1	5.0 ± 0.2
Ionian	39.00 ± 0.08	2627 ± 6	2321 ± 5	7.962 ± 0.012	14.9 ± 0.5	3.3 ± 0.1	5.0 ± 0.2
Adriatic	38.79 ± 0.13	2620 ± 6	2320 ± 7	7.954 ± 0.015	15.2 ± 0.6	3.2 ± 0.1	4.9 ± 0.2
Tyrrhenian	38.70 ± 0.03	2603 ± 3	2324 ± 2	7.926 ± 0.005	16.4 ± 0.3	3.0 ± 0.1	4.5 ± 0.1
Western	38.50 ± 0.08	2586 ± 8	2326 ± 7	7.892 ± 0.010	17.7 ± 0.5	2.8 ± 0.1	4.2 ± 0.1
Atlantic	36.03 ± 0.66	2372 ± 55	2172 ± 42	7.828 ± 0.038	19.7 ± 1.7	2.2 ± 0.2	3.4 ± 0.3
<b>DEEP</b>							
Aegean	39.05 ± 0.02	2633 ± 2	2323 ± 2	7.964 ± 0.003	14.5 ± 0.2	2.7 ± 0.2	4.1 ± 0.4
Levantine	38.78 ± 0.02	2613 ± 2	2306 ± 3	7.967 ± 0.004	14.5 ± 0.3	2.7 ± 0.2	4.1 ± 0.4
Ionian	38.77 ± 0.06	2615 ± 3	2309 ± 5	7.965 ± 0.004	14.6 ± 0.3	2.8 ± 0.2	4.2 ± 0.3
Adriatic	38.75 ± 0.04	2618 ± 3	2326 ± 5	7.940 ± 0.008	15.6 ± 0.3	2.9 ± 0.1	4.4 ± 0.2
Tyrrhenian	38.57 ± 0.05	2595 ± 5	2318 ± 2	7.923 ± 0.008	16.3 ± 0.3	2.6 ± 0.2	3.8 ± 0.2
Western	38.48 ± 0.01	2587 ± 2	2319 ± 2	7.906 ± 0.003	16.6 ± 0.2	2.5 ± 0.1	3.7 ± 0.2
Atlantic	36.10 ± 0.25	2390 ± 16	2201 ± 6	7.795 ± 0.026	21.0 ± 1.0	1.9 ± 0.1	2.9 ± 0.2
<b>BOTTOM</b>							
Aegean	–	–	–	–	–	–	–
Levantine	38.75 ± 0.01	2613 ± 2	2308 ± 1	7.969 ± 0.001	12.9 ± 0.2	2.0 ± 0.2	2.9 ± 0.3
Ionian	38.73 ± 0.001	2615 ± 2	2310 ± 2	7.965 ± 0.003	14.3 ± 0.1	2.1 ± 0.2	3.1 ± 0.3
Adriatic	–	–	–	–	–	–	–
Tyrrhenian	38.51 ± 0.01	2589 ± 3	2317 ± 1	7.916 ± 0.005	16.3 ± 0.2	2.1 ± 0.1	3.1 ± 0.2
Western	38.48 ± 0.001	2587 ± 2	2321 ± 2	7.906 ± 0.002	16.7 ± 0.1	2.1 ± 0.1	3.1 ± 0.1
Atlantic	–	–	–	–	–	–	–

**Table 3.** Mean and standard deviation values of several buffer factors in the different MedSea sub-basins and west of the Strait of Gibraltar as sampled during the M84/3 cruise. Same vertical intervals as in Table 2. The buffer factors have units of  $\text{mmol kg}^{-1}$  and Revelle is dimensionless.

	$Y_{\text{DIC}}$	$\beta_{\text{DIC}}$	$\omega_{\text{DIC}}$	$Y_{\text{TA}}$	$\beta_{\text{TA}}$	$\omega_{\text{TA}}$	Revelle
<b>SURFACE</b>							
Aegean	0.23 ± 0.01	0.28 ± 0.01	-0.37 ± 0.01	-0.28 ± 0.01	-0.31 ± 0.01	0.35 ± 0.01	9.9 ± 0.1
Levantine	0.23 ± 0.01	0.28 ± 0.01	-0.36 ± 0.01	-0.28 ± 0.01	-0.31 ± 0.01	0.35 ± 0.01	9.9 ± 0.2
Ionian	0.22 ± 0.01	0.26 ± 0.01	-0.34 ± 0.01	-0.26 ± 0.01	-0.29 ± 0.01	0.32 ± 0.01	9.8 ± 0.2
Adriatic	0.23 ± 0.01	0.27 ± 0.01	-0.35 ± 0.01	-0.27 ± 0.01	-0.30 ± 0.01	0.33 ± 0.01	10.2 ± 0.3
Tyrrhenian	0.21 ± 0.01	0.25 ± 0.01	-0.31 ± 0.01	-0.25 ± 0.01	-0.27 ± 0.01	0.30 ± 0.01	10.8 ± 0.2
Western	0.21 ± 0.01	0.25 ± 0.01	-0.31 ± 0.01	-0.25 ± 0.01	-0.27 ± 0.01	0.29 ± 0.01	10.8 ± 0.4
Atlantic	0.19 ± 0.01	0.22 ± 0.01	-0.27 ± 0.02	-0.22 ± 0.01	-0.24 ± 0.01	0.26 ± 0.02	10.3 ± 0.4
<b>INTERM.</b>							
Aegean	0.23 ± 0.01	0.28 ± 0.01	-0.35 ± 0.01	-0.28 ± 0.01	-0.30 ± 0.01	0.33 ± 0.01	10.2 ± 0.1
Levantine	0.22 ± 0.01	0.27 ± 0.01	-0.34 ± 0.01	-0.27 ± 0.01	-0.30 ± 0.01	0.33 ± 0.01	10.3 ± 0.2
Ionian	0.22 ± 0.01	0.27 ± 0.01	-0.34 ± 0.01	-0.27 ± 0.01	-0.29 ± 0.01	0.32 ± 0.01	10.4 ± 0.1
Adriatic	0.22 ± 0.01	0.27 ± 0.01	-0.33 ± 0.01	-0.27 ± 0.01	-0.29 ± 0.01	0.32 ± 0.01	10.5 ± 0.2
Tyrrhenian	0.21 ± 0.01	0.26 ± 0.01	-0.32 ± 0.01	-0.26 ± 0.01	-0.28 ± 0.01	0.30 ± 0.01	10.8 ± 0.1
Western	0.21 ± 0.01	0.24 ± 0.01	-0.30 ± 0.01	-0.24 ± 0.01	-0.26 ± 0.01	0.28 ± 0.01	11.2 ± 0.1
Atlantic	0.18 ± 0.01	0.21 ± 0.01	-0.24 ± 0.02	-0.21 ± 0.01	-0.22 ± 0.01	0.23 ± 0.02	12.2 ± 0.5
<b>DEEP</b>							
Aegean	0.22 ± 0.01	0.27 ± 0.01	-0.34 ± 0.01	-0.27 ± 0.01	-0.30 ± 0.01	0.32 ± 0.01	10.3 ± 0.1
Levantine	0.22 ± 0.01	0.27 ± 0.01	-0.34 ± 0.01	-0.27 ± 0.01	-0.29 ± 0.01	0.32 ± 0.01	10.4 ± 0.1
Ionian	0.22 ± 0.01	0.27 ± 0.01	-0.34 ± 0.01	-0.27 ± 0.01	-0.29 ± 0.01	0.32 ± 0.01	10.4 ± 0.1
Adriatic	0.22 ± 0.01	0.26 ± 0.01	-0.33 ± 0.01	-0.26 ± 0.01	-0.28 ± 0.01	0.31 ± 0.01	10.6 ± 0.1
Tyrrhenian	0.21 ± 0.01	0.25 ± 0.01	-0.31 ± 0.01	-0.25 ± 0.01	-0.27 ± 0.01	0.30 ± 0.01	10.9 ± 0.1
Western	0.21 ± 0.01	0.24 ± 0.01	-0.30 ± 0.01	-0.24 ± 0.01	-0.26 ± 0.01	0.29 ± 0.01	10.9 ± 0.1
Atlantic	0.17 ± 0.01	0.20 ± 0.01	-0.23 ± 0.01	-0.20 ± 0.01	-0.21 ± 0.01	0.22 ± 0.01	12.6 ± 0.3
<b>BOTTOM</b>							
Aegean	-	-	-	-	-	-	-
Levantine	0.20 ± 0.01	0.24 ± 0.01	-0.30 ± 0.01	-0.24 ± 0.01	-0.26 ± 0.01	0.29 ± 0.01	9.4 ± 0.1
Ionian	0.22 ± 0.01	0.27 ± 0.01	-0.33 ± 0.01	-0.27 ± 0.01	-0.29 ± 0.01	0.32 ± 0.01	10.4 ± 0.1
Adriatic	-	-	-	-	-	-	-
Tyrrhenian	0.21 ± 0.01	0.25 ± 0.01	-0.31 ± 0.01	-0.25 ± 0.01	-0.27 ± 0.01	0.29 ± 0.01	11.0 ± 0.1
Western	0.21 ± 0.01	0.25 ± 0.01	-0.30 ± 0.01	-0.25 ± 0.01	-0.27 ± 0.01	0.29 ± 0.01	11.1 ± 0.1
Atlantic	-	-	-	-	-	-	-

$$Y_{\text{DIC}} = \text{DIC} - \frac{\text{TA}_C^2}{S}$$

$$Y_{\text{TA}} = \frac{\text{TA}_C^2 - \text{DIC} \times S}{\text{TA}_C}$$

$$\beta_{\text{DIC}} = \frac{\text{DIC} \times S - \text{TA}_C^2}{\text{TA}_C}$$

$$\beta_{\text{TA}} = \frac{\text{TA}_C^2}{\text{DIC}} - S$$

$$\omega_{\text{DIC}} = \text{DIC} - \frac{\text{TA}_C \times (2 \times [\text{CO}_2] + [\text{HCO}_3^-])}{P}$$

$$\omega_{\text{TA}} = \text{TA}_C - \frac{\text{DIC} \times P}{2 \times [\text{CO}_2] + [\text{HCO}_3^-]}$$

$$S = [\text{HCO}_3^-] + 4 \times [\text{CO}_3^{2-}] + \frac{[\text{H}^+] \times [\text{B}(\text{OH})_4^-]}{K_{\text{hb}} + [\text{H}^+]} + [\text{H}^+] + [\text{OH}^-]$$

$$P = [\text{HCO}_3^-] - \frac{[\text{H}^+] \times [\text{B}(\text{OH})_4^-]}{K_{\text{hb}} + [\text{H}^+]} - [\text{H}^+] - [\text{OH}^-]$$

$$\text{TA}_C = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}]$$

$$\text{DIC} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$$

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**Table 4.** Absolute associated changes in aqueous  $[\text{CO}_2]$  ( $\mu\text{mol kg}^{-1}$ ), pH (no units) and aragonite saturation (no units) state due to several processes related to global change: a DIC increase of  $10 \mu\text{mol kg}^{-1}$  at constant TA ( $\text{CO}_2$  air–sea exchange), a decrease in calcification of  $10 \mu\text{mol kg}^{-1}$  in DIC and double in TA, a salinity increase of 0.03. Surface values from Table 2 and 3 are taken to perform the calculations.

	$\Delta[\text{CO}_2]$	$\Delta\text{pH}$	$\Delta\text{Omega}$
Air–sea $\text{CO}_2$ gas exchange			
$\Delta\text{DIC} = +10 \mu\text{mol kg}^{-1}$			
Aegean	0.56	-0.016	-0.10
Levantine	0.57	-0.016	-0.10
Ionian	0.62	-0.017	-0.07
Adriatic	0.62	-0.016	-0.10
Tyrrhenian	0.77	-0.018	-0.10
Western	0.76	-0.018	-0.10
Atlantic	0.78	-0.020	-0.10
Calcification decrease			
$\Delta\text{DIC} = +10 \mu\text{mol kg}^{-1}$			
$\Delta\text{TA} = +20 \mu\text{mol kg}^{-1}$			
Aegean	-0.36	0.011	0.11
Levantine	-0.36	0.011	0.11
Ionian	-0.40	0.012	0.11
Adriatic	-0.40	0.012	0.11
Tyrrhenian	-0.52	0.013	0.11
Western	-0.52	0.013	0.11
Atlantic	-0.53	0.015	0.11
Salinity increase			
Aegean	0.01	0.0001	0.004
Levantine	0.01	0.0001	0.004
Ionian	0.01	0.0001	0.002
Adriatic	0.01	0.0001	0.004
Tyrrhenian	0.01	0.0001	0.003
Western	0.01	0.0001	0.003
Atlantic	0.01	0.0001	0.003

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**Table 5.** Absolute associated changes in DIC concentration, pH and aragonite saturation state due several partial pressure of CO<sub>2</sub> in the atmosphere increase. The initial conditions are the mean 2011 values (Table 2).

	25 $\mu\text{atm}$	100 $\mu\text{atm}$	200 $\mu\text{atm}$	300 $\mu\text{atm}$
$\Delta\text{DIC}$ in $\mu\text{mol kg}^{-1}$				
Aegean	13.1	52.4	104.8	157.2
Levantine	13.0	52.1	104.2	156.3
Ionian	12.9	51.6	103.1	154.7
Adriatic	11.9	47.8	95.5	143.3
Tyrrhenian	9.7	38.8	77.7	116.5
Western	9.8	39.1	78.2	117.2
Atlantic	10.8	43.3	86.6	129.9
$\Delta\Omega\text{-Ar}$				
Aegean	-0.13	-0.52	-1.05	-1.57
Levantine	-0.13	-0.52	-1.04	-1.56
Ionian	-0.13	-0.52	-1.03	-1.55
Adriatic	-0.12	-0.48	-0.96	-1.43
Tyrrhenian	-0.10	-0.38	-0.76	-1.14
Western	-0.10	-0.38	-0.77	-1.15
Atlantic	-0.11	-0.43	-0.85	-1.28
$\Delta\text{pH}$				
Aegean	-0.020	-0.088	-0.199	-0.349
Levantine	-0.021	-0.089	-0.200	-0.350
Ionian	-0.022	-0.094	-0.215	-0.383
Adriatic	-0.019	-0.083	-0.186	-0.321
Tyrrhenian	-0.017	-0.073	-0.160	-0.269
Western	-0.017	-0.074	-0.164	-0.278
Atlantic	-0.022	-0.095	-0.216	-0.384

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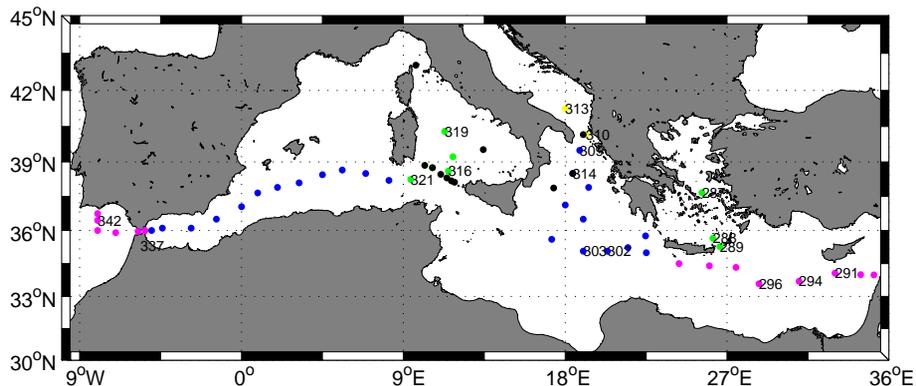
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**Fig. 1.** Map of the Mediterranean Sea with the stations from the *Meteor* M84/3 (colour dots) and *Urania* EF11 (black dots) cruises where CO<sub>2</sub> measurements were taken. The colour code for the M84/3 stations corresponds to the data showed in Figs. 12–14.

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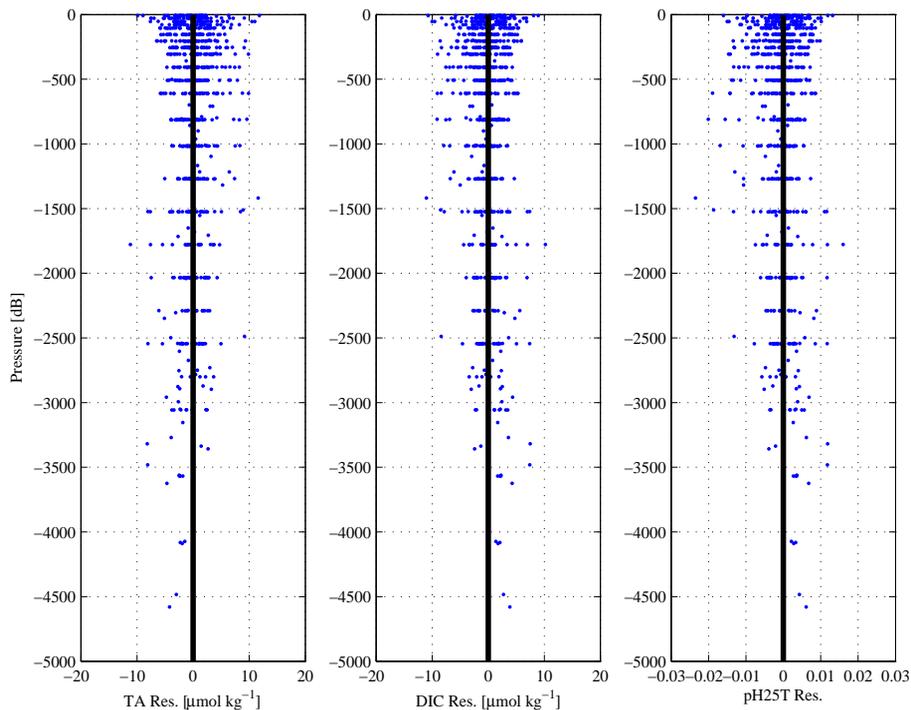
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**Fig. 2.** Vertical distribution of the residual (measured minus calculated) values for TA ( $\mu\text{mol kg}^{-1}$ ), DIC ( $\mu\text{mol kg}^{-1}$ ) and pH25T using option 4 in CO2SYS, see Table 1.

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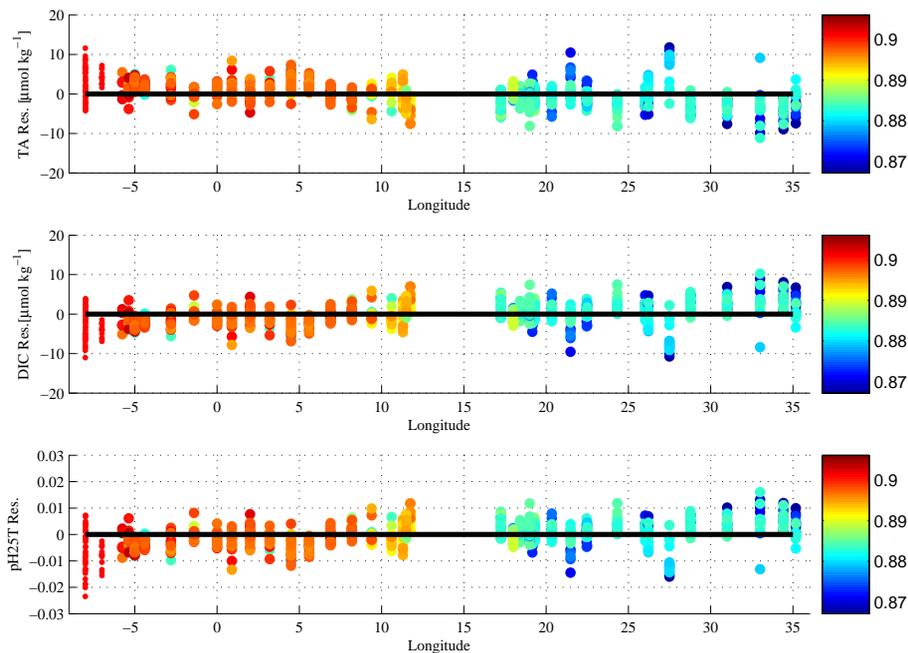
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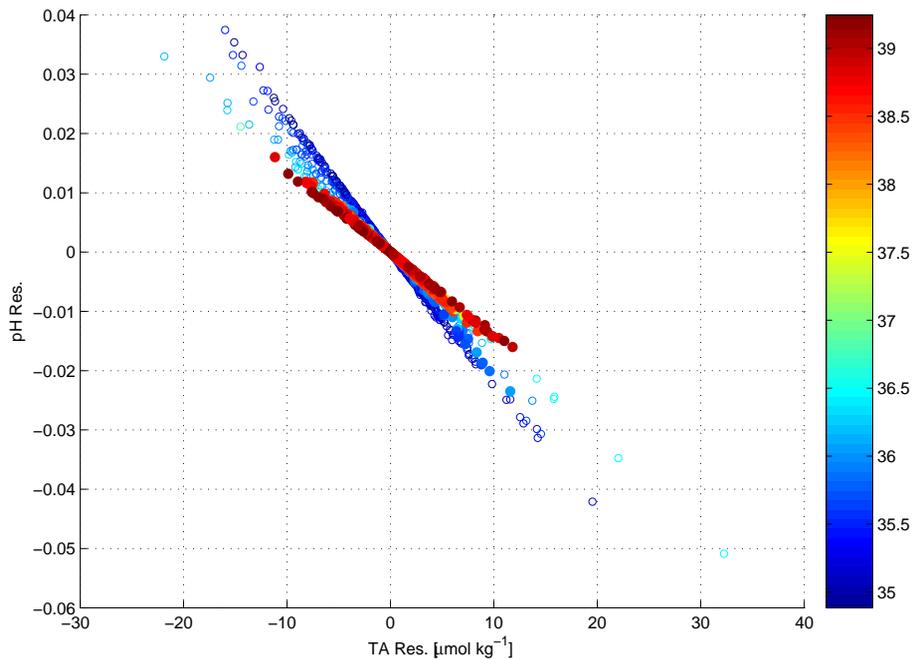
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**Fig. 3.** Same as in Fig. 2 but plotted vs. longitude. The colour code corresponds to the DIC/TA ratio. Two stations to the west of the Strait of Gibraltar were coded as red because DIC/TA ratio  $> 0.94$ .



**Fig. 4.** Relationship between the TA and pH<sub>25T</sub> residuals for the M84/3 data (filled symbols) and some CARINA cruises (open symbols). The colour code stands for salinity.

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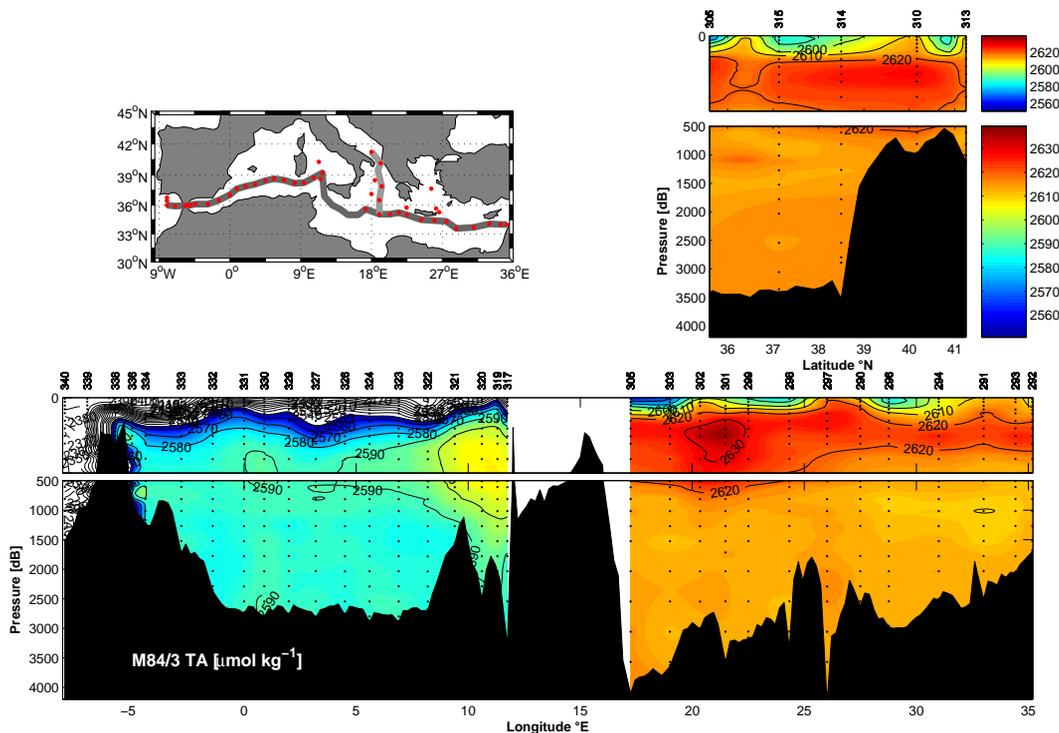
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**Fig. 5.** Sections of TA ( $\mu\text{mol kg}^{-1}$ ) in the Mediterranean Sea from the *Meteor* cruise M84/3 in April of 2011. The top right panel is a meridional section from the Adriatic Sea to the Ionian Sea (light gray line on the map) and the lower panel is the zonal section from the coast of Lebanon in the Eastern Mediterranean Sea to through the Strait of Gibraltar (dark gray line on the map). The depth scale and the colour scale are identical all both panels. The top 500 dbars in each section are slightly expanded. No stations are shown in the Atlantic due to the very different TA encountered there as compared to the Mediterranean Sea.

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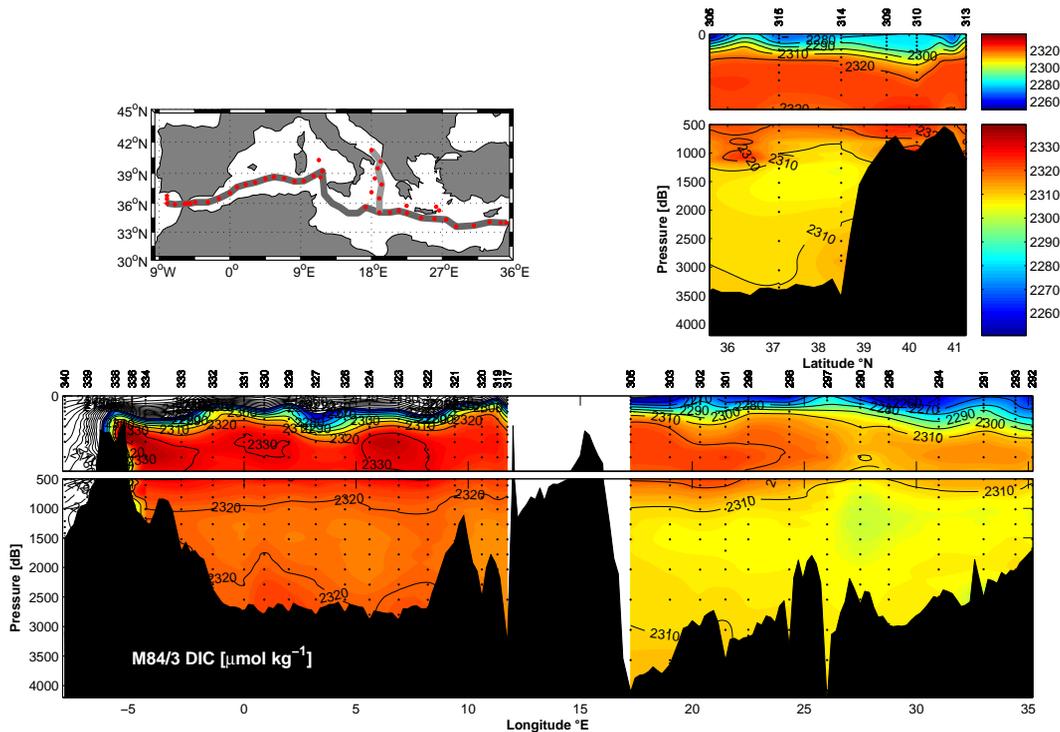
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**Fig. 6.** As in Fig. 5 but for DIC (µmol kg<sup>-1</sup>).

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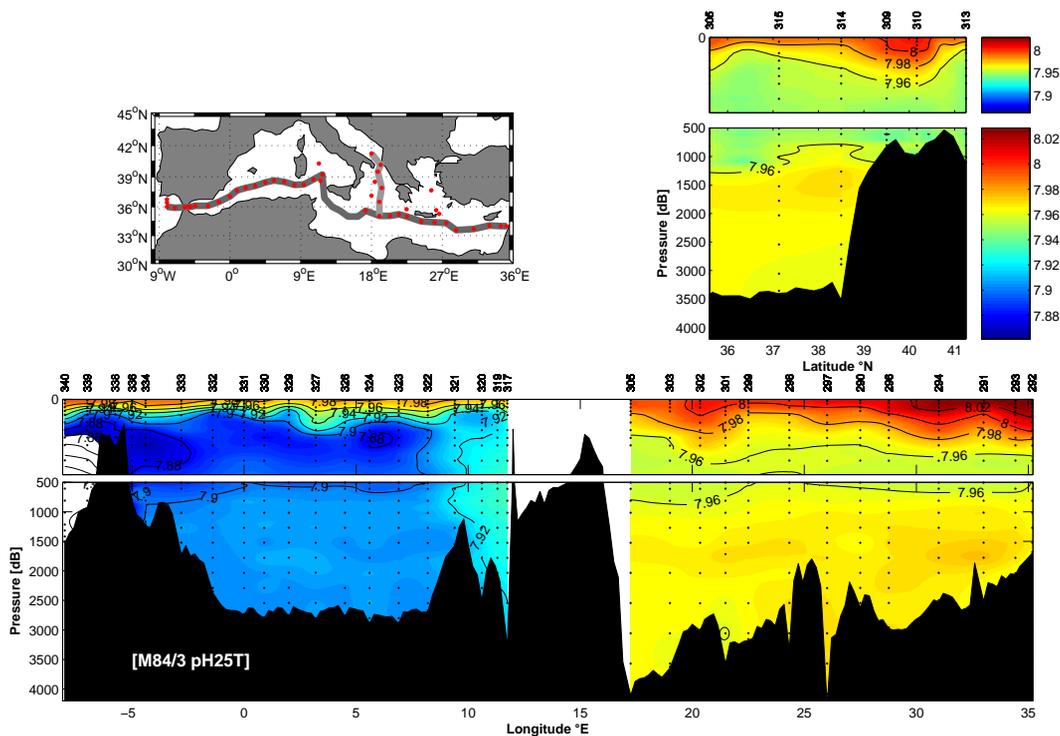


Fig. 7. As in Fig. 5 but for pH25T.

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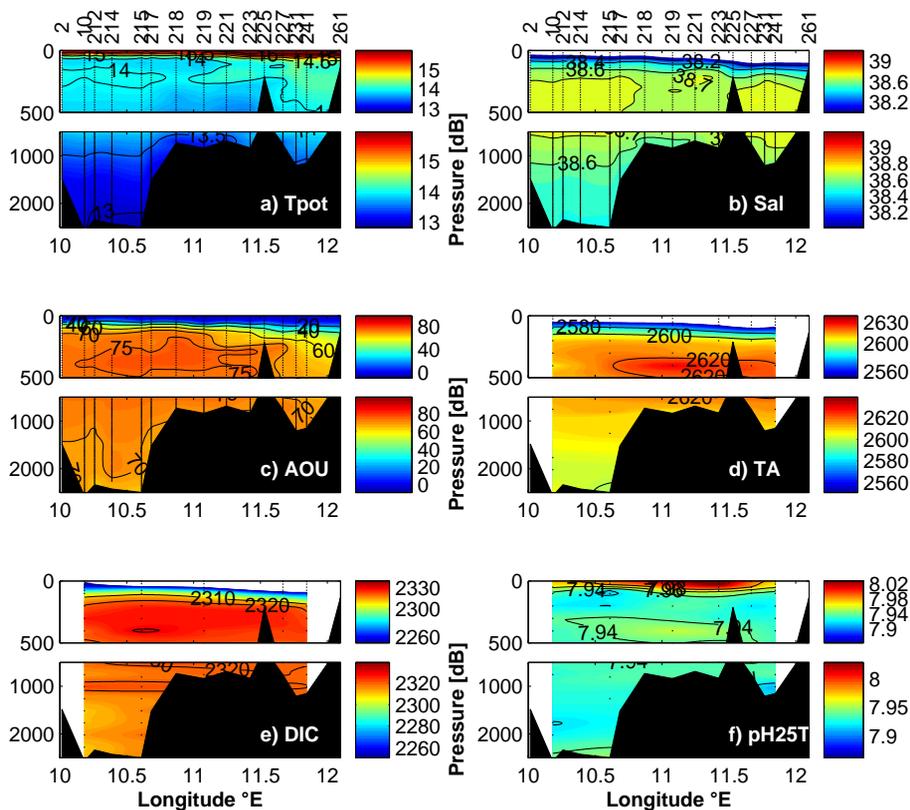
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**Fig. 8.** Vertical distributions across the Sardinia Sicily passage using EF11 data of **(a)** potential temperature ( $^{\circ}\text{C}$ ), **(b)** salinity, **(c)** Apparent Oxygen Utilization (AOU,  $\mu\text{mol kg}^{-1}$ ), **(d)** TA ( $\mu\text{mol kg}^{-1}$ ) **(e)** DIC ( $\mu\text{mol kg}^{-1}$ ) and **(f)** pH<sub>25T</sub>. Potential temperature, salinity and AOU are derived from CTD data, CTD-oxygen was calibrated with bottle data.

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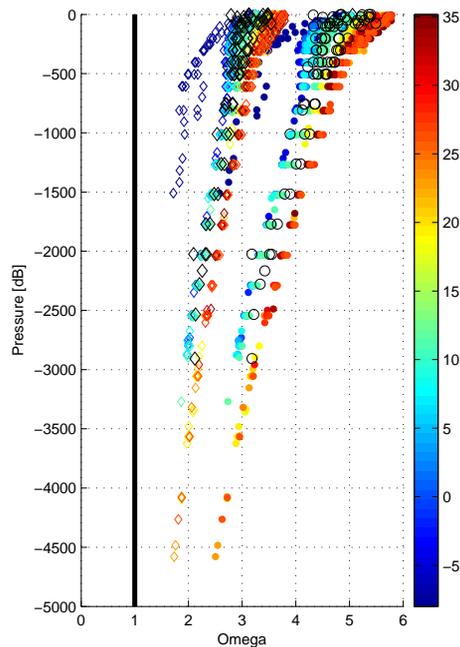
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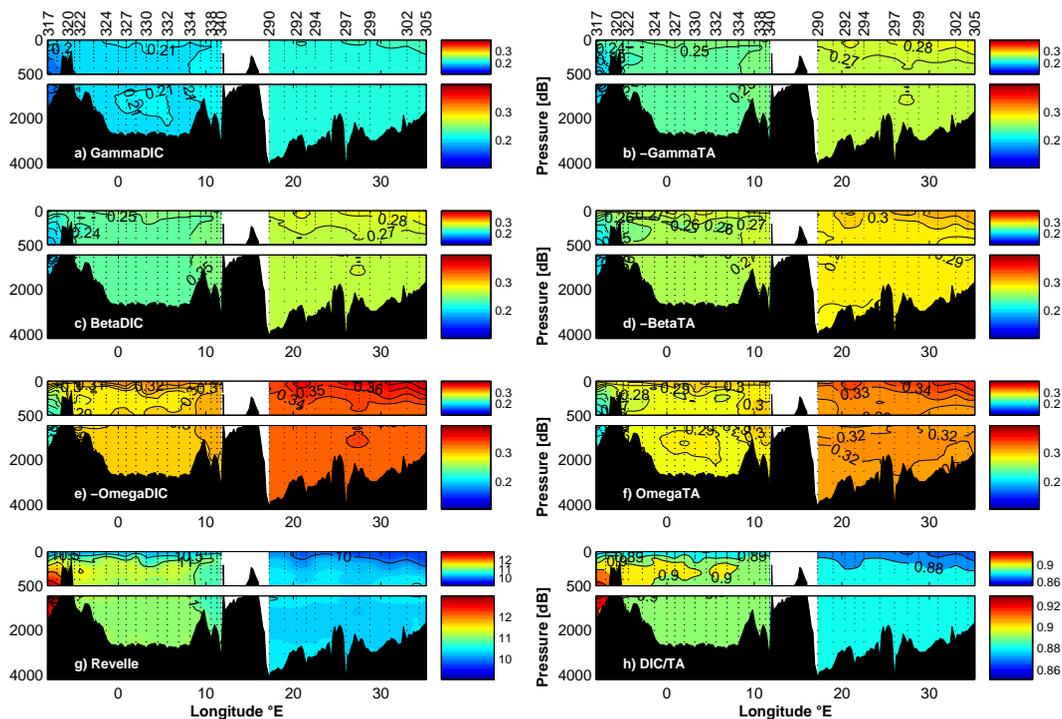
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**Fig. 9.** Vertical distribution of the carbonate saturation state for calcite (circles) and aragonite (diamonds). Data from the EF11 cruise are shown as black circles (saturation of calcite) and diamonds (aragonite). The colour code stands for longitude.

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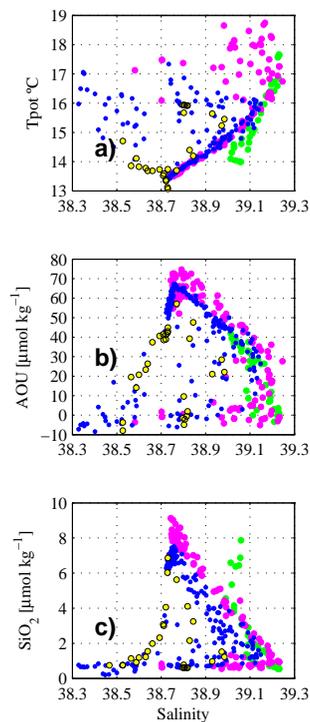


**Fig. 10.** Vertical distribution in the Mediterranean Sea from the *Meteor* cruise M84/3 of the buffer factors **(a)**  $\gamma_{\text{DIC}}$ , **(b)**  $-\gamma_{\text{TA}}$ , **(c)**  $\beta_{\text{DIC}}$ , **(d)**  $-\beta_{\text{TA}}$ , **(e)**  $-\omega_{\text{DIC}}$ , **(f)**  $\omega_{\text{TA}}$ , all in  $\text{mmol kg}^{-1}$ , **(g)** Revelle factor and **(h)** DIC/TA ratio, both dimensionless.

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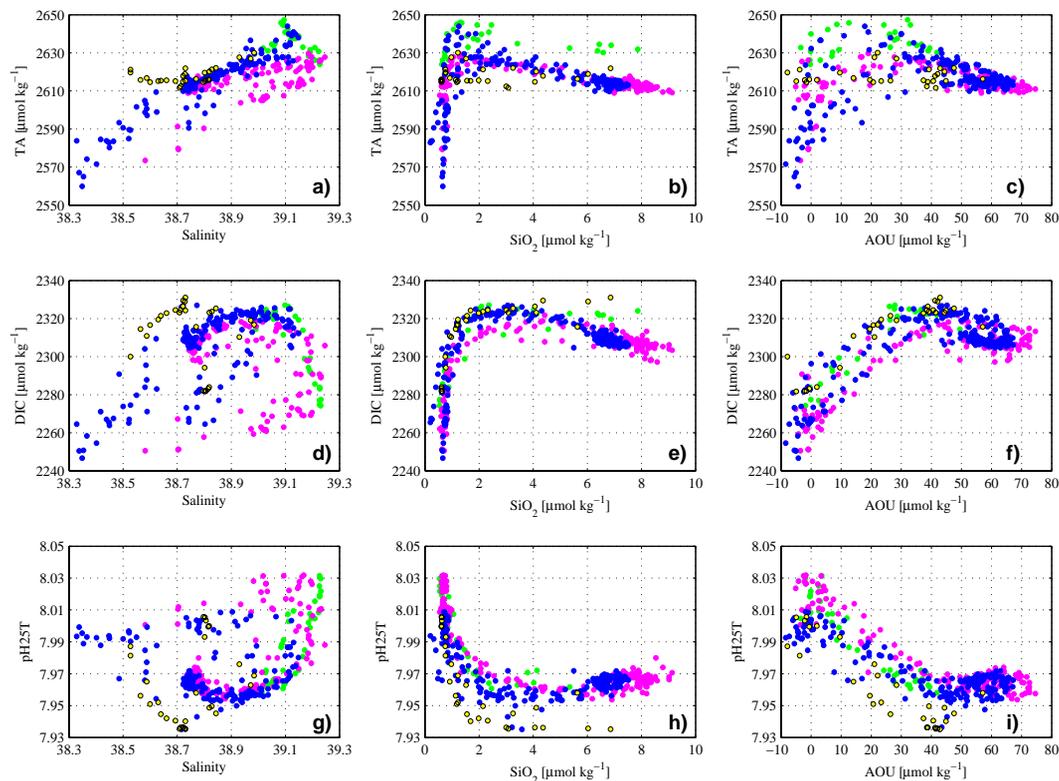


**Fig. 11.** Property–property plots for the M84/3 data in the eastern basin: Aegean Sea (green dots), Levantine basin (magenta), Ionian Sea (blue) and Adriatic Sea (yellow). **(a)** Potential temperature (°C) vs. salinity, **(b)** Apparent Oxygen Utilization (AOU in  $\mu\text{mol kg}^{-1}$ ) vs. salinity and **(c)** silicate concentration ( $\text{SiO}_2$  in  $\mu\text{mol kg}^{-1}$ ) vs. salinity. The station positions are shown in Fig. 1.

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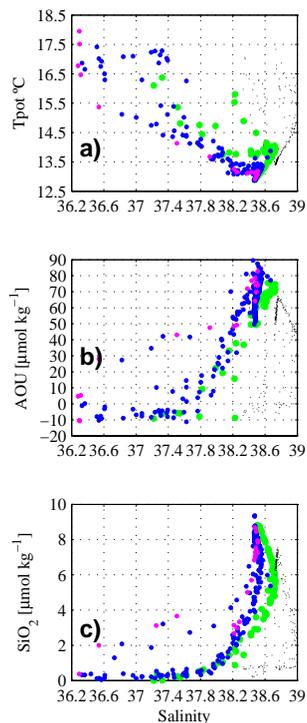


**Fig. 12.** Property–property plots for the M84/3 data in the eastern basin: Aegean Sea (green dots), Levantine basin (magenta), Ionian Sea (blue) and Adriatic Sea (yellow). First row: alkalinity (TA in  $\mu\text{mol kg}^{-1}$ ) vs. **(a)** salinity, **(b)** silicate concentration ( $\text{SiO}_2$  in  $\mu\text{mol kg}^{-1}$ ) and **(c)** AOU ( $\mu\text{mol kg}^{-1}$ ). Second row: Dissolved Inorganic Carbon (DIC in  $\mu\text{mol kg}^{-1}$ ) vs. **(d)** salinity, **(e)**  $\text{SiO}_2$  and **(f)** AOU. Third row: pH25T vs. **(g)** salinity, **(h)**  $\text{SiO}_2$  and **(i)** AOU. The station positions are shown in Fig. 1.

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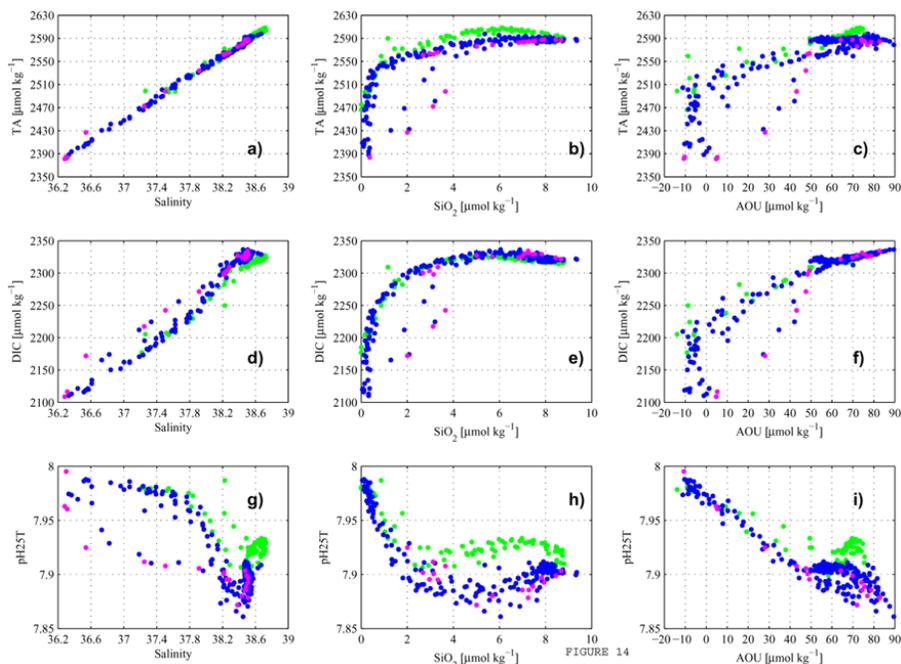


**Fig. 13.** Property–property plots for the M84/3 data in the western basin: Tyrrhenian Sea (green dots), Western basin (blue) and Strait of Gibraltar (magenta). Light black dots correspond to Ionian Sea data. **(a)** Potential temperature (°C) vs. salinity, **(b)** Apparent Oxygen Utilization (AOU in  $\mu\text{mol kg}^{-1}$ ) vs. salinity and **(c)** silicate concentration ( $\text{SiO}_2$  in  $\mu\text{mol kg}^{-1}$ ) vs. salinity. The station positions are shown in Fig. 1.

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**Fig. 14.** Property–property plots for the M84/3 data in the western basin: Tyrrhenian Sea (green dots), Western basin (blue) and Strait of Gibraltar (magenta). First row: alkalinity (TA in  $\mu\text{mol kg}^{-1}$ ) vs. (a) salinity, (b) silicate concentration ( $\text{SiO}_2$  in  $\mu\text{mol kg}^{-1}$ ) and (c) AOU ( $\mu\text{mol kg}^{-1}$ ). Second row: Dissolved Inorganic Carbon (DIC in  $\mu\text{mol kg}^{-1}$ ) vs. (d) salinity, (e)  $\text{SiO}_2$  and (f) AOU. Third row: pH25T vs. (g) salinity, (h)  $\text{SiO}_2$  and (i) AOU. The station positions are shown in Fig. 1.

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