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Water column distribution of stable isotopes and carbonate properties in the South-eastern Levantine basin (Eastern Mediterranean): Vertical and temporal change

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ABSTRACT

Water column distributions of the oxygen isotopic composition of sea-water ($\delta^{18}O_{SW}$) and the stable carbon isotope ratio of dissolved inorganic carbon ($\delta^{13}C_{DIC}$), total alkalinity (A_T) and the pH (total scale) at 25 °C ($^{25\,°C}pH_{Total}$) were investigated along the Southeast Mediterranean (SE-Med) shelf and open water, during 2009–2010. While, the vertical profiles of $\delta^{18}O_{SW}$ lacked a clear depth signature, those of $\delta^{13}C_{DIC}$ were characterized by a structure that reflects the major water masses in the Levantine basin, with noticeable vertical gradients. The $\delta^{13}C_{DIC}$ Suess effect of the Levantine water column was estimated from the difference between the average profiles of 1988 and 2009–2010 ($\Delta\delta^{13}C_{DIC}$). We observed $\delta^{13}C_{DIC}$ temporal change, which indicates propagation of anthropogenic CO_2 (C_{ant}) to depth of about 700 m. The Modified Atlantic Water (MAW; 0–200 m) and the Levantine Intermediate Water (LIW; 200–400 m) exhibited a depletion rate of -0.13 ± 0.03 and -0.11 ± 0.03‰ decade^{-1}, respectively, representing ~50% of the atmospheric change, while the deep water of the Adriatic source (700–1300 m) did not change during this period. A $\Delta\delta^{13}C_{DIC}$ depletion trend was also recognized below 1350 m, corresponding to the Aegean source deep water ($EMDW_{Aeg}$) and therefore associated to the Eastern Mediterranean Transient (EMT) event.
Anthropogenic CO_2 accumulation rate of 0.38 ± 0.12 mol C m^{-2} yr^{-1} for the upper 700 m of the SE-Med, over the last 22 yr, was estimated on the basis of mean depth-integrated $\delta^{13}C_{DIC}$ Suess effect profile. Our results confirm lower accumulation rate than that of the subtropical North Atlantic, resulting due to the super-saturation with respect to CO_2 of the well-stratified Levantine surface water. High pCO_2 saturation during summer (+150 µatm), in oppose to a small degree of under-saturation in winter (−30 µatm) was calculated from surface water A_T and $^{25\,°C}pH_{Total}$ data. However, the $\delta^{13}C_{DIC}$ depletion trend of the LIW and the $EMDW_{Aeg}$ supports isotopically light C_{ant} penetrating into the Levantine interior during convection events, such as the EMT.

1. Introduction

The Eastern Mediterranean, in particular the Levantine basin, is one of the most evaporative marginal seas in the world — a crucial area in the larger framework of the Mediterranean conveyor belt (Millot and Taupier-Letage, 2005; Pinardi and Masetti, 2000; Tanhua et al., 2013). The water body in this region is both stratified and ultra-oligotrophic, due to the advection of low salinity, nutrients-poor Modified Atlantic Water (MAW) and limited freshwater input (Béthoux et al., 1999; Hecht, 1992). Hence, this region is an ideal location to investigate water column temporal and vertical changes, occurring on relative short time scales, annual to decadal.

The importance of the Levantine basin to the formation of mid-depth Levantine Intermediate Water (LIW) was described by Hecht et al. (1988). This water mass evolves from down-welling of saline surface water, the Levantine Surface Water (LSW), during the winter, and eventually circulates through the Gibraltar strait to high latitudes of the Atlantic ocean at depths around 1000 m, contributing heat, salt and mass to northward transport in the Atlantic (Bigg et al., 2003). Two deep water masses are currently observed below the LIW: the Eastern Mediterranean deep water (EMDW) from an Adriatic source ($EMDW_{Adr}$) and below it the EMDW from an Aegean source ($EMDW_{Aeg}$; Kress et al., 2014; Roether et al., 1996). Several studies have addressed in details the impact of the Eastern Mediterranean Transient (EMT) event on the hydrological properties of the Eastern Mediterranean (Klein et al., 1999; Roether et al., 1996, 2007). According to these studies, the current deep water stratigraphy reflects a switch in the deep

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water formation from the Adriatic to the Aegean that occurred during the early 1990's. Recent analysis of the oceanographic characteristics of the Eastern Mediterranean over the last three decades by Cardin et al. (2015) shows that the state of the EM deep water structure is still far from the pre-EMT conditions, as observed by the signature of the alternation of the two dense water sources, Adriatic and Aegean.

The Mediterranean Sea is considered a region capable of absorbing a considerable amount of anthropogenic CO_2 (C_{ant}) per unit area. Its high total alkalinity (Copin-Montégut, 1993; Cossarini et al., 2015; Schneider et al., 2007) gives it greater chemical capacity to take up C_{ant} (Álvarez et al., 2014). Furthermore, its deep waters are ventilated on relatively short time scales (ca. 100 yr; Schneider et al., 2014; Stöven and Tanhua, 2014), allowing penetration of C_{ant} (Palmiéri, et al., 2015; Schneider et al., 2010). Anthropogenic CO_2 however, cannot be measured directly because the anthropogenic component cannot be distinguished from the much larger natural background (Palmiéri, et al., 2015). Instead, it has been estimated indirectly from observable physical and biogeochemical quantities (Schneider et al., 2010; Touratier and Goyet, 2009, 2011). Recent studies have reported that carbon of anthropogenic origin with a total of 1.0–1.7 Pg C had entered the Mediterranean water column, where 52% are from the air–sea flux and 48% are from the Atlantic water inflow (Palmiéri, et al., 2015; Schneider et al., 2010). It has been proposed that the Mediterranean Sea will experience amplified acidification relative to the global average surface ocean, based on the TrOCA approach (El Rahman Hassoun et al., 2015; Touratier and Goyet, 2011) or acidification similar to the global-ocean average based on a thermodynamic model by Palmiéri et al. (2015). On a sub-basin scale more knowledge is still needed to fully understand the carbonate system distribution on decadal time resolution to better estimate the C_{ant} uptake of this region.

The oxygen isotopic composition of sea-water ($\delta^{18}O_{SW}$) and the stable carbon isotope ratio of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in seawater have been widely used as tracers in oceanographic research (*e.g.*, Craig and Gordon, 1965; Kroopnick, 1985; Rohling and Bigg,

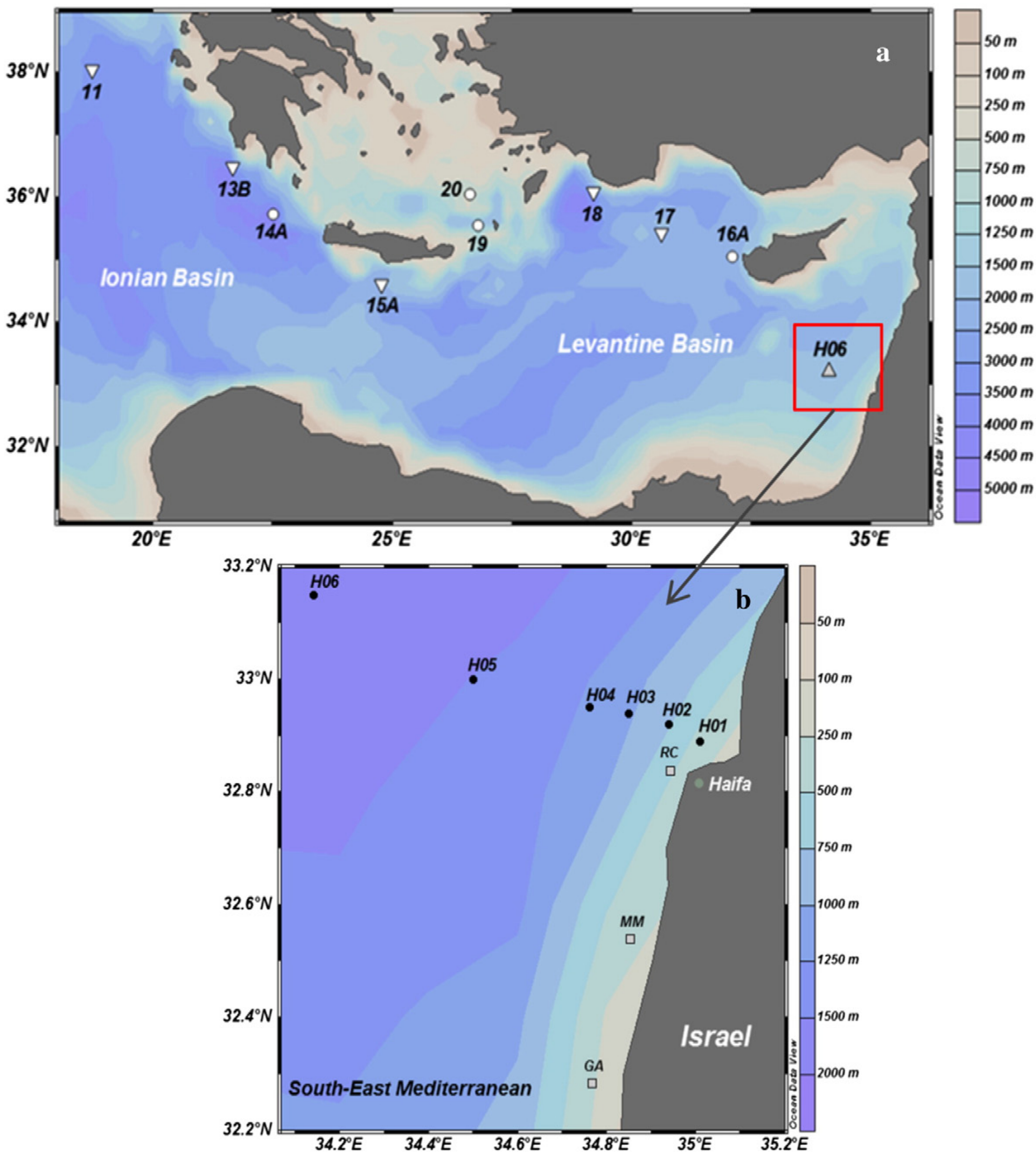

Fig. 1. (a) Rosette and surface stations investigated along the Ionian and Levantine sub-basins, during the survey of 1988 (Pierre, 1999) and the current study sampling scheme denoted by the deepest sampling station HO6. (b) The current study sampling scheme: rosette and surface stations along the SE-Med shelf and open water.