



Calcium distribution in the subtropical Atlantic Ocean: Implications for calcium excess and saturation horizons



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ABSTRACT

This study constituted the first attempt to measure dissolved calcium ($[Ca^{2+}]_{meas}$) in the subtropical North Atlantic, during a zonal transoceanic cruise along 24.5°N (WOCE A05 section), in summer 1992. $[Ca^{2+}]_{meas}$ was obtained in 20 full-depth equidistant stations along the section, showing that their gradients are rather sensitive to horizontal and vertical water mass distribution. Deep waters along 24.5°N systematically show a positive calcium excess of $20 \pm 14 \mu\text{mol} \cdot \text{kg}^{-1}$, i.e., more $[Ca^{2+}]$ than expected by CaCO_3 dissolution and organic matter oxidation (estimated by total alkalinity and nitrate). CaCO_3 settling and benthic dissolution accounts for 70% and the North Atlantic plus Arctic riverine inputs of HCO_3^- for the remaining 30%. Combining $[Ca^{2+}]_{meas}$ and CO_2 data sets, carbonate mineral saturation states distributions for aragonite and calcite can be obtained. The two solubility ratios resulted, on average, 0.5% smaller than if conservative behavior for Ca^{2+} was assumed (an approach widely followed when $[Ca^{2+}]_{meas}$ is unknown). As a result, shallower saturation horizon depths for both carbonate states (19 dbar for aragonite and 10 dbar for calcite) are yielded if $[Ca^{2+}]_{meas}$ is taken into account instead than estimated from salinity.

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1. Introduction

Carbon dioxide (CO_2) emissions are distributed among the atmosphere, the ocean, and the terrestrial biosphere (Sitch et al., 2015). The oceanic sink has contributed to the uptake of about one third of all anthropogenic CO_2 emissions produced in the last three centuries (Khatiwala et al., 2013). In particular, the North Atlantic basin is considered to contain 23% of the global oceanic anthropogenic CO_2 (Sabine et al., 2004) and so, to be crucial in its entrance and balancing in the whole ocean. Once CO_2 is in solution, dissolved inorganic carbon (C_T) levels rise and chemical balances of the CO_2 system in seawater are affected leading to the formation of hydrogen ions that lower seawater pH while consuming carbonate (CO_3^{2-}) ions. The CO_3^{2-} controls the rate of calcium carbonate (CaCO_3) precipitation and dissolution in the ocean, which in turn determine the amount of carbon that is potentially buried in the sediments on geological timescales. Hence, there exists the possibility of inducing a decrease in the atmospheric CO_2 removing capacity of the ocean as a consequence of the continuous oceanic entrance of atmospheric CO_2 (Feely et al., 2004). However, how marine carbon

cycle will evolve under a climate change scenario is still one of the main issues in Ocean Sciences (Sabine and Tanhua, 2009).

The World Ocean Circulation Experiment (WOCE), as a part of the World Climate Research Programme (WCRP), was the first attempt to study physical processes that affect oceanic circulation and are responsible for climate variability globally. The inclusion of systematic physical and chemical measurements within a network of selected repeat hydrographic sections has allowed scientists to describe trends in different seawater parameters worldwide. The WOCE section A05, across 24.5°N in the North Atlantic subtropical gyre (Fig. 1A), has been occupied several times since 1957. In 1992, the section was included in the WOCE Project and high spatial resolution *in situ* CO_2 system measurements were made for the first time. Since then, five occupations have been conducted, in 1992, 1998, 2004, 2010, and 2011, providing a great opportunity to analyze natural and anthropogenic CO_2 meridional fluxes and quantify changes in pH and in the carbon budget in the North Atlantic. The main findings regarding the variability of the CO_2 system across 24.5°N are reported in the works of Macdonald et al. (2003), Rosón et al. (2003), Brown et al. (2010), and Guallart et al. (2015a, 2015b). The WOCE section A05 was carried out between 14 July and 15 August 1992 along 24.5°N on board R/V Hespérides from Cadiz (Spain) to Miami (Florida, USA). Full-depth CTD profiles were performed at 107 hydrographic stations. At each station, water samples were taken at selected depths for different chemical analyses as salinity, oxygen, nutrients, chlorofluorocarbons (CFCs), pH, TA, C_T , primary

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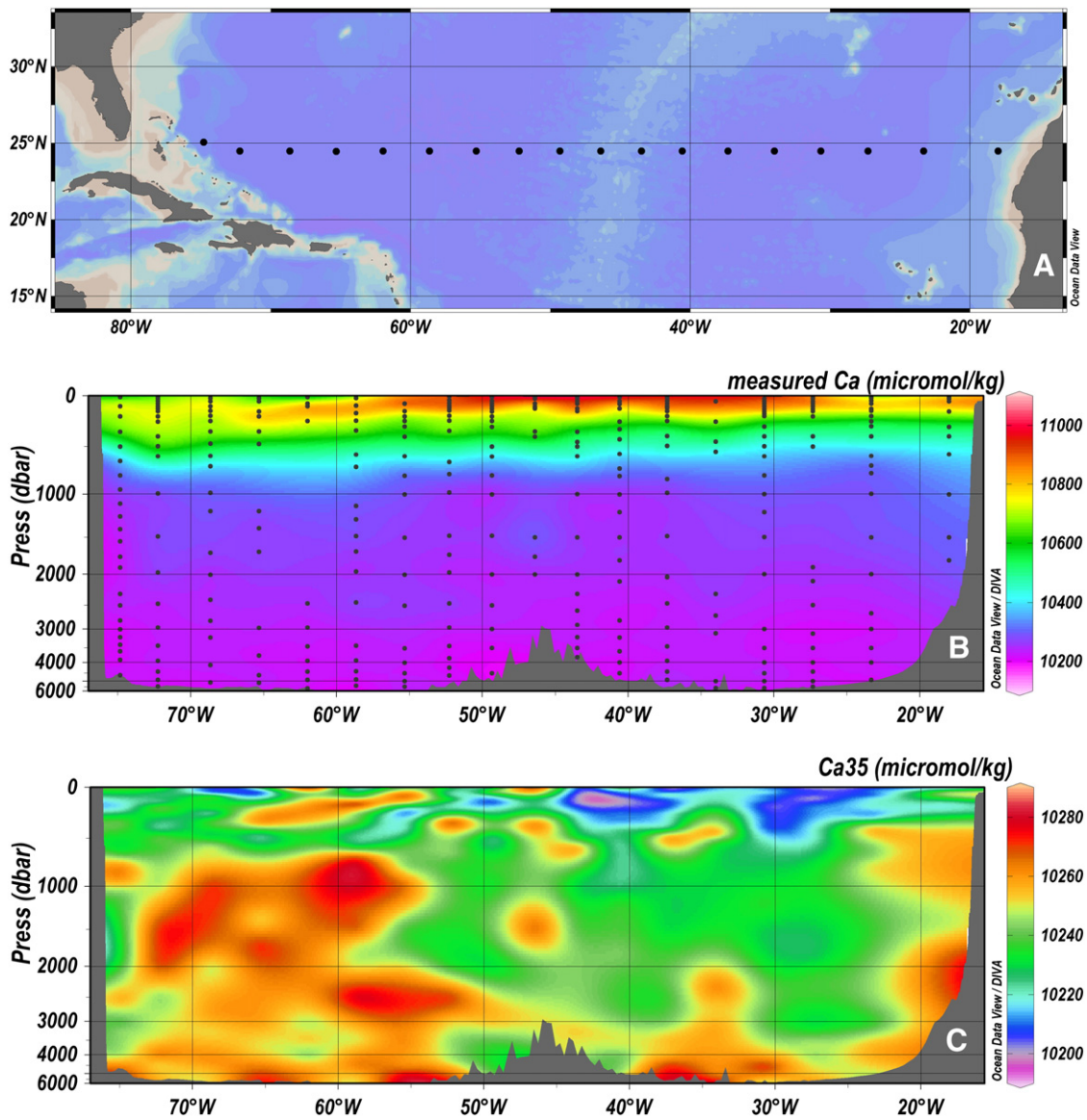


Fig. 1. (A) Map of the sampling stations along 24.5°N in the Atlantic. (B) Calcium concentration distribution. Points show sampling bottles. (C) Calcium concentration normalized to salinity 35. Vertical scales are stretched in order to enhance the upper waters distributions.

production, Al, and radiocarbon (^{14}C). Additionally, and being the only time with respect to the following occupations, calcium ($[\text{Ca}^{2+}]$) samples were collected at 18 stations (one in six, Fig. 1A) in 1992. Prior studies in the studied region and other oceans often made Ca^{2+} measurements ($[\text{Ca}^{2+}]_{\text{meas}}$) in one-time sampling or scattered stations (Krumgalz, 1982), but this is the first time that direct and systematic $[\text{Ca}^{2+}]_{\text{meas}}$ were made along an entire transoceanic section. This effort allows obtaining a real picture of the distribution of $[\text{Ca}^{2+}]$ along the section and, more important, not inferred by indirect approaches.

Combining CO_3^{2-} and Ca^{2+} measurements, the degree of saturation of seawater with respect to calcite and aragonite can be calculated by means of their respective carbonate mineral saturation state or solubility ratio, defined as

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}} \quad (1)$$

where $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$ is the ionic concentration product (ICP) and K_{sp} , (θ, S, P) is the apparent solubility product for calcite or aragonite (two common mineral phases of CaCO_3), respectively, both taken from Mucci

(1983) but considering the pressure correction for calcite and aragonite from Ingle (1975) and Millero (1979). $\Omega < 1$ represents the thermodynamic conditions for undersaturation, which favors dissolution of carbonate minerals. On the contrary, $\Omega > 1$ means oversaturation conditions, which favors precipitation. The depth where $\Omega = 1$ is named saturation horizon. To apply Eq. (1) in practice, historically neither $[\text{CO}_3^{2-}]$ nor $[\text{Ca}^{2+}]$ has been directly measured. Despite the current development of direct techniques for measuring $[\text{CO}_3^{2-}]$ (Byrne and Yao, 2008), it is commonly calculated from direct measurements of two of the four CO_2 variables (C_T , TA, pH, $f\text{CO}_2$), in our case TA and pH. Regarding $[\text{Ca}^{2+}]$, since it is one of the eleven major ions in seawater, its concentration is often calculated indirectly by means of the historical assumption that it shows a quasi-conservative behavior, i.e., its concentration is proportional to salinity: $[\text{Ca}^{2+}]_{\text{calc}} = [\text{Ca}^{2+}]_{35} \cdot S/35 \mu\text{mol} \cdot \text{kg}^{-1}$ and any deviations from this behavior are not taken into account. The term $[\text{Ca}^{2+}]_{35}$ indicates the Ca^{2+} concentration at a fixed salinity of 35 and was assumed to be “constant,” but showing varying values according to different authors (e.g., $10,277 \mu\text{mol} \cdot \text{kg}^{-1}$ by Culkin and Cox (1966), $10,287 \mu\text{mol} \cdot \text{kg}^{-1}$ by Riley and Tongudai (1967)). More recently, Dickson et al. (2007) and Millero et al. (2008) give an average of both values ($10,282 \mu\text{mol} \cdot \text{kg}^{-1}$) for reference composition of seawater.

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