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. $[Ca^{2+}]_{meas}$ were 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 datasets, 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 behaviour 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.

Keywords: calcium; alkalinity; aragonite; calcite; seawater; North Atlantic.

1 INTRODUCTION

Carbon dioxide (CO₂) 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 CO₂ 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 CO₂ (Sabine *et al.*, 2004) and so, to be crucial in its entrance and balancing in the whole ocean. Once CO₂ is in solution, dissolved inorganic carbon (C_T) levels rise and chemical balances of the CO₂ system in seawater are affected leading to the formation of hydrogen ions that lower seawater pH while consuming carbonate (CO₃²⁻) ions. The CO₃²⁻ controls the rate of calcium carbonate (CaCO₃) 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 CO₂ removing capacity of the ocean as a consequence of the continuous oceanic entrance of atmospheric CO₂ (Feely *et al.*, 2004). But, 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* CO₂ 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 CO₂ meridional fluxes and quantify changes in pH and in the carbon budget in the North Atlantic. The main findings regarding the variability of the CO₂ 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.* (2015). 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 production, Al and radiocarbon (¹⁴C). Additionally, and being the only time with respect to the following occupations, calcium ([Ca²⁺]) samples were collected at 18 stations (one in six, Fig. 1A) in 1992. Prior studies in the studied region and other oceans often made Ca²⁺ measurements ([Ca²⁺]_{meas}) in one-time sampling or scattered stations (Krumgalz, 1982), but this is the first time that direct and systematic [Ca²⁺]_{meas} were made along an entire transoceanic section. This effort allows obtaining a real picture of the distribution of [Ca²⁺] along the section and, more important, not inferred by indirect approaches.

Combining CO₃²⁻ and Ca²⁺ 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:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K'_{sp}} \quad [1]$$

where $[Ca^{2+}][CO_3^{2-}]$ 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 CaCO₃) respectively, both taken from Mucci (1983) but considering the pressure correction for calcite and aragonite from Ingle (1975) and Millero (1979). Ω<1 represents the thermodynamic conditions for undersaturation, which favours dissolution of carbonate minerals. On the contrary, Ω>1 means oversaturation conditions, which favours precipitation. The depth where Ω=1 is named saturation horizon. To apply eqn. [1] in practice, historically neither [CO₃²⁻] nor [Ca²⁺] have been directly measured. Despite the current development of direct techniques for measuring [CO₃²⁻] (Byrne and Yao, 2008), it is commonly calculated from direct measurements of two of the four CO₂ variables (C_T, TA, pH, fCO₂), in our case TA and pH. Regarding [Ca²⁺], 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 behaviour, i.e. its concentration is proportional to salinity: [Ca²⁺]_{calc}=[Ca²⁺]₃₅·S/35 μmol·kg⁻¹ and any deviations from this behaviour are not taken into account. The term [Ca²⁺]₃₅ indicates the Ca²⁺ concentration at a fixed salinity of 35 and was assumed to be “constant”, but showing varying values according to different authors (e.g. 10277 μmol·kg⁻¹ by Culkin and Cox (1966), 10287 μmol·kg⁻¹ by Riley and Tongudai (1967)). More recently Dickson et al (2007) and Millero *et al.* (2008) give an average of both values (10282 μmol·kg⁻¹) for reference composition of seawater. However, currently it is well known that [Ca²⁺] shows small but distinguishable variations that cannot be explained only by salinity itself, as they are mainly related to the formation/dissolution of CaCO₃ particles

(representing about 0.5-1.5% of total $[Ca^{2+}]$, Cao and Dai, 2011). In order to take into account the influence of such variability in the solubility ratio, in this study $[Ca^{2+}]$ is directly measured with a sensitive method. In other words, we re-examine the general assumption that variability of the ratio $[CO_3^{2-}]/K'_{sp}$ primarily governs the degree of saturation (Chung *et al.*, 2003). This approach will allow us to compare Ω by means of eqn. [1], obtained either from observations and calculations from salinity.

Hence, the goals of this paper are a) to outline the zonal distribution of $[Ca^{2+}]$ in the water masses of the subtropical North Atlantic Ocean, b) to assess the excess of $[Ca^{2+}]$ of deep water masses with respect to $CaCO_3$ dissolution and its implications at basin scale, and c) to quantify the input of $[Ca^{2+}]_{meas}$ both in the degree of saturation of seawater and in the apparent vertical displacement of the calcite and aragonite saturation horizons.

2 MATERIAL AND METHODS

2.1 Carbonate system measurements

Full depth profiles of TA and pH were obtained on 107 stations. As reported in Rosón *et al.* (2003), pH was measured potentiometrically on the National Bureau of Standards (NBS) scale, with a combined glass electrode associated to a temperature probe (Perez and Fraga, 1987a), achieving a shipboard precision of 0.005 units, according to 184 replicate analysis corresponding to two different oceanographic bottles fired at the same depth at each station (Ríos and Rosón, 1996). TA measurements were made by titration of seawater with potentiometric endpoint detection (Perez and Fraga, 1987b), reaching a precision of $\pm 2 \mu\text{mol}\cdot\text{kg}^{-1}$. The measured pH and TA and calculated C_T data from pH and TA were checked by means of a secondary quality control (2ndQC) following the procedures used in CARINA (CARbon IN the Atlantic) (Tanhua *et al.*, 2010). However, since CDIAC pH data are reported on the seawater scale and referenced to 25°C, the measured pH_{NBS} was converted to the seawater scale (SWS) and referenced to 25°C before undergoing 2ndQC. The change in scale was performed keeping invariable C_T and A_T . The 2ndQC performed is the best indicator of the consistency of pH, TA and C_T data with respect to other datasets, and thus of their accuracy. After the analysis, the pH_{SWS} data were bias adjusted according to CARINA recommendations because their offset almost doubled the recommended threshold (0.005 units) for a minimum adjustment (Tanhua *et al.*, 2010) and, in order to avoid a new bias in the new calculated C_T due to the reduction of pH values without changing TA, the obtained TA correction was also taken into account despite not surpassing the recommended threshold (further details in Guallart *et*

al. (2013)). By doing this, the newly calculated C_T data from bias adjusted pH and TA were certainly kept invariable with respect to the original C_T data, which had shown a very low offset after 2ndQC (only $1 \mu\text{mol kg}^{-1}$). The new C_T data was recalculated by using dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987) and the boric acid constant of Dickson (1990). The revised dataset was reported to CDIAC together with a report of the quality control performed (Guallart et al., 2013). The reported data set has already been used in more recent works (Guallart et al., 2015a; Guallart et al., 2015b; Zunino et al., 2015).

2.2 Ca^{+2} measurements

Ca^{+2} samples were collected in plastic bottles of 150 ml after sampling 18 full depth profiles along the A05 section (315 samples, Fig. 1A). They were stored at room temperature for two months and analysed on land, immediately after the cruise. Dissolved $[\text{Ca}^{+2}]$ was determined in the lab, after weighting the water sample, by classic volumetric titration with Ethylene Glycol Tetraacetic Acid (EGTA, $\sim 0.18 \text{ M}$) as titrant and borax as buffer, with end-point potentiometric detection, using a *Metrohm* calcium selective electrode. The method is described in Lebel and Poisson (1976) and Kanamori and Ikegami (1980). A $[\text{Ca}^{+2}]$ standard ($9800 \mu\text{mol}\cdot\text{kg}^{-1}$) was prepared dissolving $2.01328 \pm 0.00001 \text{ g}$ of pure CaCO_3 in a $2000.0 \pm 0.5 \text{ ml}$ analytical flask. To reach the seawater ionic strength, $58.262 \pm 0.001 \text{ g NaCl}$ and $10.698 \pm 0.001 \text{ g MgCl}_2$ (both free of calcium impurities) were also added. Before making up to the flask mark, several additions of 0.5 ml of $\text{HCl } 12 \text{ N}$ (up to 6.5 ml) were done to ensure the complete CaCO_3 dissolution. The salinity of this standard was 35.359. The reproducibility ($\pm$ one sigma) over 12 standard samples was $\pm 7 \mu\text{mol}\cdot\text{kg}^{-1}$. Additionally, in order to obtain a more robust check of the precision, about five samples of a substandard of 25 l of seawater ($S=34.405$) were analyzed among each station batch, giving global value of $\pm 10 \mu\text{mol}\cdot\text{kg}^{-1}$ for 60 samples.

3 RESULTS AND DISCUSSION

3.1 $[\text{Ca}^{+2}]$ distribution along A05 section

Fig. 1B shows the $[\text{Ca}^{+2}]_{\text{meas}}$. Its distribution is very similar to salinity (Bryden *et al.*, 1996). Waters in the upper 150 dbar are enriched in $[\text{Ca}^{+2}]_{\text{meas}}$ due to an excess of evaporation over the subtropical gyre. Intermediate waters ($\sim 1000 \text{ dbar}$) have two influences: toward lower $[\text{Ca}^{+2}]_{\text{meas}}$ due to the northward penetration of Antarctic Intermediate Water (AAIW, mainly in the western section) and toward high $[\text{Ca}^{+2}]_{\text{meas}}$ due to the mixing with Mediterranean Water coming out of the Strait of Gibraltar (in the eastern side of the section). North Atlantic Deep

Water (NADW, roughly 1500-3500 dbar) includes two limbs (whose respective origins are located in the Labrador and the Greenland-Iceland-Norwegian seas), which show indistinguishable features with respect their $[Ca^{+2}]_{meas}$ levels. Finally, the Antarctic Bottom Water (AABW, >4000 dbar) is restricted to the western flank of the Mid-Atlantic Ridge showing the lowest $[Ca^{2+}]_{meas}$.

Figure 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.

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178 In order to remove the effect of salinity in $[\text{Ca}^{2+}]$, this parameter is often normalized at a fixed
179 salinity (often 35). Hence, $\text{Ca}_{35} = [\text{Ca}^{2+}]_{\text{meas}} \cdot S / 35$, where S is the measured salinity related to the
180 Niskin bottle where the calcium sample was taken (Fig. 1C). The highest values ($\text{Ca}_{35} > 10280$
181 $\mu\text{mol} \cdot \text{kg}^{-1}$) found within bottom waters in the western boundary are associated with the core
182 of AABW, around 5000 dbar). Another Ca_{35} maximum is associated to the core of AAIW (~1000
183 dbar), which is also more evident in the western side of the section. This distribution is due to
184 the fact that at this latitude this water mass is younger in the west than in the east, according
185 to its general circulation (Reid, 1994) in which AAIW mainly circulates along the western
186 boundary and then travels to the eastern subtropical North Atlantic. With respect to the core
187 of NADW, distinguishable differences arise between the eastern and the western basins. There
188 are not many systematic $[\text{Ca}^{2+}]_{\text{meas}}$ reported in the literature for the western basin. Only de
189 Villiers (1998) reports data from a single station in the northwestern basin (GEOSECS #24,
190 53.76°N , 33.63°W) showing a value of $10210 \mu\text{mol} \cdot \text{kg}^{-1}$ at 2500 dbar, which is very low
191 compared with those reported in this study due to its northern location.

192 A plot of $[\text{Ca}^{2+}]_{\text{meas}}$ versus salinity, for all samples ($n=315$), is shown in Fig. 2A. The intercept of
193 the linear regression (with $r^2=0.992$) was assumed null. The slope means specific calcium:
194 $\text{Ca}^{+2}/S = 292.5 \pm 1.1 \mu\text{mol} \cdot \text{kg}^{-1} \cdot \text{‰}^{-1}$. This ratio is 0.4% lower than the averaged value obtained by
195 Culkin and Cox (1966) who analysed 9 samples over North Atlantic ($293.6 \mu\text{mol} \cdot \text{kg}^{-1} \cdot \text{‰}^{-1}$, Fig.
196 2A blue straight line). It is also 0.5% lower than reported by Riley and Tongudai (1967) over 81
197 samples collected in all seas ($293.9 \mu\text{mol} \cdot \text{kg}^{-1} \cdot \text{‰}^{-1}$). It is clear that, for the North Atlantic, the
198 estimation from Culkin and Cox (1996) overestimates $[\text{Ca}^{2+}]$ if conservative behaviour of $[\text{Ca}^{2+}]$
199 is invoked. Therefore, packages that compute seawater carbonate chemistry should include an
200 option so that measured instead of calculated calcium can be used when computing calcium
201 carbonate saturation states.

Figure 2A: Linear regression (black line) of measured $[\text{Ca}^{2+}]_{\text{meas}}$ versus salinity for all the water samples ($n=315$) collected in WOCE-A5 cruise. Blue line shows the reference line obtained by both Culkin and Cox (1966) or Riley and Tongudai (1967) frequently that are used for indirect estimation of the calcium concentration via salinity in sysCO2 programs.

$[\text{Ca}^{2+}]_{\text{calc}}$ is in excess with respect to $[\text{Ca}^{2+}]_{\text{meas}}$ in all depths (Fig. 2B). The differences between the two profiles range from $74 \mu\text{mol}\cdot\text{kg}^{-1}$ in upper waters to $25 \mu\text{mol}\cdot\text{kg}^{-1}$ in bottom waters ($50 \mu\text{mol}\cdot\text{kg}^{-1}$ on average). Horizontal bars are smaller for deep waters (2000-5700 dbar, $\pm 12 \mu\text{mol}\cdot\text{kg}^{-1}$ on average) than for upper waters ($\pm 20 \mu\text{mol}\cdot\text{kg}^{-1}$) due to the weaker variability of abyssal waters. Despite that, this weak variability is mainly supported by $[\text{Ca}^{2+}]_{\text{meas}}$ due to the better precision (but not better accuracy) of salinity versus $[\text{Ca}^{2+}]_{\text{meas}}$. The precision of salinometers assures 0.005 or less, i.e. $2 \mu\text{mol}\cdot\text{kg}^{-1}$ in $[\text{Ca}^{2+}]_{\text{calc}}$, while the analysis of calcium gives $10 \mu\text{mol}\cdot\text{kg}^{-1}$.

The mean vertical profile of Ca_{35} is shown in Fig. 2C. For comparison, reported values for single stations by de Villiers (1998) in the equatorial and northern North Atlantic, respectively, are also shown for reference. Waters in the upper 150 dbar are relatively poor in Ca_{35} mainly due to biologically induced CaCO_3 precipitation. This process is favoured by the oversaturation of both aragonite and calcite in this layer, since solubility ratios are higher than 4 and 6, respectively. Ca_{35} increases towards deeper levels, showing a relatively high dispersion mainly due to the zonal variability already pointed out. This result is known since Dittmar (1884), who

222 used precise analyses of 77 samples of the Challenger expedition all over the world oceans and
 223 stated that $\text{Ca}^{2+}/\text{Cl}^-$ ratio is higher in deep waters than in surface waters.

224
 225 Figure 2B: Vertical profile of the differences between averaged calculated calcium
 226 ($[\text{Ca}^{2+}]_{\text{calc}} = 293.6 \cdot S$, according to Culkin and Cox (1966)) and measured calcium ($[\text{Ca}^{2+}]_{\text{meas}}$) for
 227 315 seawater samples collected in WOCE-A5 cruise. Horizontal bars indicate zonal variability
 228 ($\pm\sigma_{\text{Ca}}$). Vertically averaged difference is $50 \pm 23 \mu\text{mol} \cdot \text{kg}^{-1}$.

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Figure 2C: Mean vertical profile of $[Ca_{35}]=[Ca]/S \cdot 35$ (Calcium concentration normalized to salinity=35, in $\mu\text{mol}\cdot\text{kg}^{-1}$), for 315 seawater samples collected in WOCE-A5 cruise. Horizontal bars indicate zonal variability ($\pm\sigma_{Ca}$). Vertical bars indicate pressure range of each zonal mean ($\pm\sigma_p$). Triangles and squares are data reported from single stations by de Villiers (1998) in the equatorial and northern North Atlantic, respectively.

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238 3.2 Ca²⁺ excess in deep Atlantic waters

239 It is well known that CaCO₃ dissolution in deep oceans leads to changes in both normalized
240 Ca²⁺ and alkalinity (Brewer *et al.*, 1975) according to the solubility reaction $\text{CaCO}_3(\text{s}) \rightarrow \text{Ca}^{2+} +$
241 CO_3^{2-} . Hence, one mole of dissolved carbonate produces one mole of excess of calcium and
242 two equivalents of alkalinity excess. The two changes are also related with the proton
243 exchanges associated with oxidative decomposition of organic matter in the deep ocean,
244 which also causes nitrate production. If the correction for the produced NO₃⁻ is taken into
245 account in TA, assuming a constant stoichiometric ratio between dissolution and organic
246 remineralization, we can state (Chung *et al.*, 2003):

$$247 \quad \Delta Ca_{35} = 0.5 \cdot \Delta TA_{35} + 0.53 \cdot \Delta NO_3^- \quad [2]$$

248 where the symbol Δ means changes with respect to preformed values, i.e., the initial values of
249 the main endmember in the North Atlantic between 1300 and 5000 m (NADW) before mixing
250 with others in the deep ocean. A discussion about the choice of the preformed values reported
251 by de Villiers (1998) will be followed here. It is consistent with direct measurements of
252 $[\text{Ca}^{2+}]_{\text{meas}}$, TA and NO₃⁻ in the aforementioned station close to the NADW source region
253 (GEOSECS #24, 53.76°N, 33.63°W: 10214, 2311 and 17 $\mu\text{mol}\cdot\text{kg}^{-1}$, respectively) in the depth
254 range of this water mass at that latitude (800–2500 m). Hence, “Calcium excess” can be
255 calculated as:

$$256 \quad Ca_{\text{EX}} = \Delta Ca_{35} - 0.5 \cdot \Delta TA_{35} - 0.53 \cdot \Delta NO_3^- \quad [3]$$

257 Positive values for Ca_{EX} mean $[\text{Ca}^{2+}]_{\text{meas}}$ is in excess than expected from CaCO₃ dissolution and
258 organic matter oxidation, while negative values mean $[\text{Ca}^{2+}]_{\text{meas}}$ is in deficit. The mean vertical
259 profile of Ca_{EX} is shown in Fig. 3. There is an excess of calcium in all depths, with the maxima
260 excess centered at the core of NADW (2500 m). Below this level, Ca_{EX} are lower but increase
261 toward the sea floor, suggesting that much of the calcium comes from benthic dissolution. In
262 fact, the higher Ca_{EX} values appear to be close to the calcite (4500 dbar) and aragonite (2500
263 dbar) saturation horizons. Averaged over the 1300–5000 m depth range (132 samples), Ca_{EX} is
264 $20 \pm 14 \mu\text{mol}\cdot\text{kg}^{-1}$ along the A05 section. This robust result supports the idea that at basin scale
265 the North Atlantic requires extra sources of Ca²⁺. According to similar results at only one
266 station in the equatorial Atlantic and comparing Ca²⁺ with δHe^3 profiles, de Villiers (1998)

267 argues that the mechanism that mainly accounts for this difference is the low-temperature
 268 hydrothermal input from the mid-ocean ridge. Unfortunately, no He^3 measurements were
 269 made in any occupation of the A05 section in order to confirm the hydrothermal hypothesis.
 270 Main differences between Ca_{EX} values at 5°S reported by de Villiers (1998) and those obtained
 271 in this paper (figure 3) are $13 \mu\text{mol}\cdot\text{kg}^{-1}$, which are mainly affected by the precision of our
 272 measurements ($\pm 10 \mu\text{mol}\cdot\text{kg}^{-1}$).

Figure 3: Black: Vertical profile of zonally averaged Calcium excess. Horizontal bars indicate zonal variability ($\pm\sigma_{\text{CaEX}}$). Red: Calcium excess reported by de Villiers (1998) in the equatorial North Atlantic (5°S, 25°W) for comparison.

We can estimate the fraction of this Ca_{EX} that is originated by the contribution of HCO_3^- dissolved in rivers in the drainage area. For this purpose, we only consider the contribution of river discharges in the Northern hemisphere, assuming that river runoff to the southern hemisphere do not contribute directly to Meridional Overturning Circulation (MOC). The averaged HCO_3^- river flux that runoff to the North Atlantic + Arctic basin is estimated to be of 94.2 $\text{TgC}\cdot\text{y}^{-1}$ (Ludwig *et al.*, 1996). If all this water were incorporated into NADW and distributed into the Atlantic Ocean through MOC (with a mean flow rate of 19 ± 6 Sv, Cunningham *et al.*, 2007), this yields a maximum contribution of Ca_{EX} coming from the Arctic Rivers runoff of 6 ± 2 $\mu\text{mol}\cdot\text{kg}^{-1}$. Hence, this upper limit contribution accounts for one third of the observed Ca_{EX} at 24,5°N.

Other contributions to the calcium accumulation include carbonate dissolution, both from particles in the water column (as they settle) or by benthic dissolution from the sea floor. Berelson *et al.* (2007) concluded that approximately 80–90% of the alkalinity excess in deep waters can be explained by benthic dissolution, particle settling being a minor source of the TA excess in the deep ocean. In fact, in the Sargasso Sea the reported carbonate fluxes are from the sediments into the water column ($0.12\text{--}0.37$ $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, Hales *et al.*, 1994). Using a large amount of high-quality alkalinity data of the water column, Chung *et al.* (2003) estimated an averaged carbonate dissolution rate in the deep waters of the whole Atlantic Ocean on 0.05 $\mu\text{mol CaCO}_3$ $\text{kg}^{-1}\cdot\text{yr}^{-1}$. Combining this result with the NADW circulation age of 288 yr estimated with radiocarbon tracer data by Matsumoto (2007), deep calcium excess estimated by benthic dissolution yields 14 $\mu\text{mol}\cdot\text{kg}^{-1}$. This contribution accounts for the remaining two thirds of the observed Ca_{EX} at 24.5°N.

3.3 Changes in saturation horizon depth

The degrees of saturation obtained by using $[\text{Ca}^{2+}]_{\text{meas}}$ instead of $[\text{Ca}^{2+}]_{\text{calc}}$ in equation [1] are smaller on average over the whole section ($n=317$), being $0.5\pm0.2\%$ for aragonite and $0.3\pm0.1\%$ for calcite. Surface waters show values around 4 and 6, respectively (not shown), but the degree of saturation of the two mineral forms decreases with depth mainly because their solubility increases with pressure and drops with both temperature and pH (Chung *et al.*,

2003). Close to the saturation horizons, the dependence with pressure is linear (Fig. 4). Here, the approach used (i.e. using $[\text{Ca}^{2+}]_{\text{meas}}$ or $[\text{Ca}^{2+}]_{\text{calc}}$) is critical for the calculation of the depth at which saturation horizon ($\Omega=1$) is reached for both mineral phases.

In order to estimate the average horizons of aragonite and calcite along the section, the solubility ratios were fitted to a straight line against pressure $\Omega=a+b\cdot P$, in the vicinity of $\Omega=1$. The pressure at which $\Omega=1$ can be obtained knowing the regression parameters as: $P_{\Omega=1} = (1 - a)/b$. For aragonite, we consider the range $0.8 < \Omega < 1.2$ ($n=71$, Fig. 4A) and for calcite, $0.7 < \Omega < 1.3$ ($n=61$, Fig. 4B). Table 1 shows the results for both phases using respectively $[\text{Ca}^{2+}]_{\text{calc}}$ or $[\text{Ca}^{2+}]_{\text{meas}}$. The meaning of coefficients should be taken as integrated along the zonal A05 section. Hence, the deviations from $P_{\Omega=1}$ are mainly associated to zonal variability. For aragonite the average difference between the two horizons over the section is 19 dbar, 14 dbar for calcite. In both crystal varieties, saturation horizons are located shallower for $[\text{Ca}^{2+}]_{\text{meas}}$ than for $[\text{Ca}^{2+}]_{\text{calc}}$.

Phase	Calcium database	n	a=Intercept	b=Slope ($\cdot 10^4, \text{dbar}^{-1}$)	P($\Omega=1$) (dbar)	ΔP (dbar)
Aragonite (fig. 4A)	Calculated	71	1.511 ± 0.002	-2.00 ± 0.03	2552 ± 54	19
	Measured	71	1.505 ± 0.002	-1.99 ± 0.03	2533 ± 55	
Calcite (fig. 4B)	Calculated	61	1.995 ± 0.003	-2.21 ± 0.04	4511 ± 97	14
	Measured	61	1.986 ± 0.003	-2.19 ± 0.04	4497 ± 96	

Table 1. Results of the linear regressions $\Omega=a+b\cdot P$ in the vicinity of $\Omega=1$ for both Calcium carbonate phases with $[\text{Ca}^{2+}]_{\text{calc}}$ or $[\text{Ca}^{2+}]_{\text{meas}}$. All fits yield the same determination coefficient: $R^2=0.98$.

Although the precision of $[\text{Ca}^{2+}]$ estimated via salinity (modern salinometers ensure an accuracy of 0.005 that yields less than $2 \mu\text{mol}\cdot\text{kg}^{-1}$ in $[\text{Ca}^{2+}]_{\text{calc}}$) is much better than that provided by titration ($10 \mu\text{mol}\cdot\text{kg}^{-1}$), in this paper we have shown that $[\text{Ca}^{2+}]_{\text{calc}}$ from a conservative $[\text{Ca}^{2+}]/S$ ratio is biased with respect to measured $[\text{Ca}^{2+}]$ (up to $74 \mu\text{mol}\cdot\text{kg}^{-1}$ in upper waters, $50 \mu\text{mol}\cdot\text{kg}^{-1}$ on average). This bias propagates a relative overestimation of 0.5% in the calculation of the solubility ratio with respect to the same parameter calculated with $[\text{Ca}^{2+}]_{\text{meas}}$. Although this difference is not critical in most of the water column, it could have important implications reaching close to the aragonite and calcite saturation horizons, since it diagnoses a deeper estimation of the saturation horizon. In any case, the biases due to change

in calcium concentrations does not constitute a major uncertainty in the calculation of saturation indices. In fact, they remain relatively small compared with uncertainties result of include different formulations of thermodynamic constants. As a best example, our systematic bias for the aragonite saturation horizon (19 dbar) is three times smaller than that from using the boron-to-salinity ratio from Lee et al. (2010) instead of that from Uppström (1974), as discussed by Orr et al (2015). Orr and Epitalon (2015, fig 12A) show that this bias yields about 60 dbar, also upwards, at North Atlantic subtropical latitudes. Our calcium biases (0.5%) are also small when compared with uncertainty in calculated carbonate ion concentration originating from the analytical error of pH (± 0.005 , i.e. 1.1% in $[\text{CO}_3^{2-}]$), while error in total alkalinity ($\pm 2 \mu\text{mol}\cdot\text{kg}^{-1}$) yield only 0,1% in $[\text{CO}_3^{2-}]$.

The deviations of Ω nearby 100% saturation horizons (at 2500 dbar for aragonite and at 4500 dbar for calcite) can be estimated from table 1 in 0.010 and 0.015 respectively. These may be compared with the random errors for the two mineral phases associated with current uncertainties both in equilibrium thermodynamic constants as well as with the two CO_2 measured parameters, being $\Delta\Omega_{\text{arag}} = \pm 0.067$ and $\Delta\Omega_{\text{calc}} = \pm 0.110$ at $P_{\text{v}=1}$ (Chung *et al.*, 2003). These figures yield corresponding uncertainties in saturation horizons of ± 300 m and ± 470 m respectively. Our results give uncertainties between 15 and 30 times smaller. In conclusion, systematic errors from using calculated instead of measured calcium induce a 10-15% of additional uncertainty in the determination of solubility ratios as well as 3-6% in the determination of saturation horizons in the vicinity of $P_{\text{v}=1}$.

Figure 4. Plots of aragonite (A) and calcite (B) mineral saturation state in the vicinity of the saturation horizons, including $[Ca^{2+}]_{calc}$ (blue) and $[Ca^{2+}]_{meas}$ (red) in equation [1]. Regression lines correspond to equations [4] to [7].

4 CONCLUSIONS

A systematic positive excess of Ca^{2+} with respect to CaCO_3 dissolution and organic matter oxidation of $20 \pm 14 \mu\text{mol} \cdot \text{kg}^{-1}$ is found in subtropical deep waters of the Atlantic Ocean. Our results are consistent with the finding by de Villiers (1998) that the deep Atlantic contains higher levels of dissolved Ca^{2+} (or smaller levels of total alkalinity) at basin scales than expected from CaCO_3 dissolution only. The North Atlantic plus Arctic riverine inputs of HCO_3^- account for up to 30% of the calcium excess while CaCO_3 settling and its benthic dissolution account for the remaining 70%.

Considering vertical and zonal averaged values of the subtropical North Atlantic, $[\text{Ca}^{2+}]$ calculated under the assumption that is conservative is $50 \pm 23 \mu\text{mol} \cdot \text{kg}^{-1}$ higher than observed $[\text{Ca}^{2+}]$. This difference makes that the ionic concentration product and, thus, the degree of saturation of seawater with respect to calcite and aragonite to be $0.5 \pm 0.2\%$ higher on average when using Ca^{2+} values estimated from salinity than observed $[\text{Ca}^{2+}]$. This bias has relevant implications nearby aragonite and calcite saturation horizons since it propagates a deeper estimation of these horizon depths (19 and 14 dbar respectively). These biases are smaller when compared with the uncertainties related both with the precision of the two selected carbonic system variables to measure and also with the choice of set of thermodynamic constants of carbonic system (mainly affecting to the boron constant). However, the direct measurement of calcium reduces these errors up to 3-6% for saturation horizons and 10-15% for solubility ratios. Scientists interested in calcium carbonate saturation states should take into account these results and consider measuring calcium instead of using the universal ratios reported by Culkin and Cox (1966) or Riley and Tongudai (1967). In the same way, we encourage programmers of seawater carbon software packages to allow direct input of $[\text{Ca}^{2+}]_{\text{meas}}$, in order to gain accuracy and minimize biases in the solubility ratios of carbonate minerals. Alternatively, we propose a new value of the relationship between $[\text{Ca}^{2+}]$ and salinity that should be programmed instead of the universal ratio in the subtropical North Atlantic ($292.5 \mu\text{mol} \cdot \text{kg}^{-1} \cdot \text{‰}^{-1}$). Universal ratios should be re-evaluated in other basins.

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