Inorganic carbon and pH levels in the Rockall Trough 1991-2010

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Inorganic carbon and pH levels in the Rockall Trough 1991-2010, (in press). Deep Sea Research.

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Abstract

The accumulation of anthropogenic CO_2 in the oceans is altering seawater carbonate chemistry. Monitoring carbonate parameters is therefore necessary to understand potential impacts on ocean ecosystems. Total alkalinity (A_T) and dissolved inorganic carbon (C_T) were sampled across the Rockall Trough in Feb 2009 (CE0903) and Feb 2010 (CE10002) as part of a baseline study of inorganic carbon chemistry in Irish shelf waters. The results have been compared with data from WOCE surveys A01E (Sept 1991), A01 (Dec 1994), AR24 (Nov 1996), and A24 (June 1997). The 2009 and 2010 datasets provide a baseline of inorganic carbon and acidity levels in surface waters of the Rockall Trough in late winter for future comparison. The temporal evolution of anthropogenic carbon (ΔC_{ant}) between the 1990s and 2010 was evaluated using two separate methods; (i) a comparison of the concentrations of C_T between surveys, after correcting it for remineralisation and formation and dissolution of calcium carbonate ($\Delta C_{T\text{-}abio}$) and (ii) an extended Multiple Linear Regression was used to calculate the ΔC_{ant} between 1991 and 2010 (ΔC_{ant}^{eMLR}). There was an increase in $\Delta C_{T\text{-}abio}$ and ΔC_{ant}^{eMLR} of 18±4μmol kg^{-1} and 19±4μmol kg^{-1}, respectively, in the subsurface waters between 1991 and 2010, equivalent to a decrease of 0.040±0.003 pH units over the 19 year period. There was an increase in both $\Delta C_{T\text{-}abio}$ and ΔC_{ant}^{eMLR} of 8±4μmol kg^{-1} in Labrador Sea Water (LSW) in the Trough between 1991 and 2010, and LSW has acidified by 0.029±2 pH units over the same time period. A reduction in calcite and aragonite saturation states was observed, which may have implications for calcifying organisms in the region.

1. Introduction

The world's oceans have taken up close to half of the accumulated anthropogenic fossil fuel emissions since the Industrial Revolution, buffering even more serious climate change (Sabine et al., 2004). When CO_2 reacts with seawater, chemical changes occur that result in a decrease in ocean pH, a process referred to as ocean acidification. Research into oceanic carbon uptake and storage is necessary to understand impacts on ocean ecosystems, along with the need to predict future storage capacity and subsequent effects on global climate. The North Atlantic is an important sink of atmospheric CO_2 (Takahashi et al., 2002). While a number of papers have described the carbonate signature of the water masses in the North Atlantic (e.g. Olafsson et al., 2009; Pérez et al., 2010; Ríos et al., 2001; Stoll et al., 1996; Tanhua et al., 2006), an extensive study had yet to be carried out in the Rockall Trough. This oceanic region is an important area in climate research as it provides a pathway for warm saline waters of the upper North Atlantic to reach the Nordic Seas, where they are continually cooled resulting in deep water formation as part of the global thermohaline circulation (Ellett and Martin, 1973; Holliday et al., 2000). The water column in the Trough has a complex structure due to the presence of several water masses with different origins and histories and is therefore well suited for the study of carbonate chemistry. This area also hosts a vast array of cold water coral structures, interacting with a range of water masses along the continental margin, Rockall Bank and Porcupine Bank (De Mol et al., 2002; Roberts et al., 2003; Wheeler et al., 2011). These organisms are sensitive to any change in pH (Orr et al., 2005), and therefore this region provides a natural laboratory to study the effects of ocean acidification on deep water ecosystems.

Carbon in the ocean is present in both inorganic and organic forms, either dissolved or particulate. The focus of this paper is on the inorganic part of the oceanic carbon cycle, which is quantitatively the dominant form of carbon present in seawater. Zeebe and Wolf-Gladrow (2003) described the processes that affect the carbon chemistry of a water mass; dissolved inorganic carbon (C_T) levels change due to air-sea interaction between the atmosphere and surface waters, where C_T distribution is temperature-dependent with increased CO_2 solubility in colder waters, and also decreasing solubility with increasing salinity. Respiration of organic matter and dissolution of $CaCO_3$ in the water column tend to increase C_T concentrations, while photosynthesis and formation of calcium carbonate ($CaCO_3$) in surface layers reduces C_T levels. Total alkalinity decreases with $CaCO_3$ formation, while it increases with the dissolution of $CaCO_3$, with a slight increase with photosynthesis. A_T is not affected by CO_2 exchange with the atmosphere, concentrations are generally governed by factors that affect salinity (Broecker and Peng, 1982; Lee et al., 2006) and it is found to behave conservatively in surface waters of the major oceans (Lee et al., 2006; Millero et al., 1998a).

An important link to the global carbon cycle is the formation and dissolution of $CaCO_3$ which effectively neutralizes the acidification effect of CO_2 absorbed by the oceans (Zeebe and Wolf-Gladrow, 2003); such that $CaCO_3$ formation in surface waters, its sinking and re-dissolution at depth, effectively transfers CO_2 from the surface to deep waters (Millero, 2007). Many organisms in the ocean depend on $CaCO_3$ to lay down their shells or skeletons, made of either calcite or aragonite depending on the species. $CaCO_3$ solubility tends to increase with depth and the saturation horizon refers to the depth below which calcite or aragonite is under-saturated ($\Omega<1$). A number of studies have found that dissolution of $CaCO_3$ can occur above the saturation horizon (e.g. Chen, 2002; Feely et al., 2004; Milliman et al., 1999); however it may not be a significant process in the North Atlantic (Friis et al., 2006a; Friis et al., 2006b). Aragonite is more soluble than calcite and the aragonite saturation horizon (ASH) occurs at shallower depths, ~3500m deep in the North Atlantic (Feely et al., 2004). A shoaling of the saturation horizons is expected in the oceans due to increasing C_T, which may have detrimental effects on marine ecosystems (Feely et al., 2004; Orr et al., 2005).

C_T and A_T were measured in water samples collected across the Rockall Trough in February of 2009 and 2010, close to the end of the winter mixing period. Körtzinger et al. (2008) reported maximum C_T in March marking the end of winter mixing. Since biological activity is at a minimum during winter, it is possible to describe ‘preformed’ carbonate conditions in the upper water column, useful when trying to detect any changes due to increasing atmospheric CO_2. Results were compared to similar WOCE transects across the Trough in Sept 1991 (A01E), Dec 1994 (A01), Nov 1996 (AR24) and June 1997 (A24), Fig. 1. Our goal here is to characterise the carbonate parameters in the different water masses in the Rockall Trough region, and to identify any changes over the 19 year period since the WOCE transects were made. The recent paper by McGrath et al. (2012), which describes the nutrient and oxygen characteristics of the water masses in the 2009/10 surveys and compares them with those encountered in the WOCE 1996 survey, sets the background for the chemical properties of the water masses in the Trough.

2. Method

The main data sets presented here were collected during two surveys on the RV Celtic Explorer to the Rockall Trough, one in February 2009 and one in February 2010. WOCE data were extracted from the CDIAC database (https://cdiac.ornl.gov/oceans/). See Figure 1 and Table 1 for details on all surveys discussed.

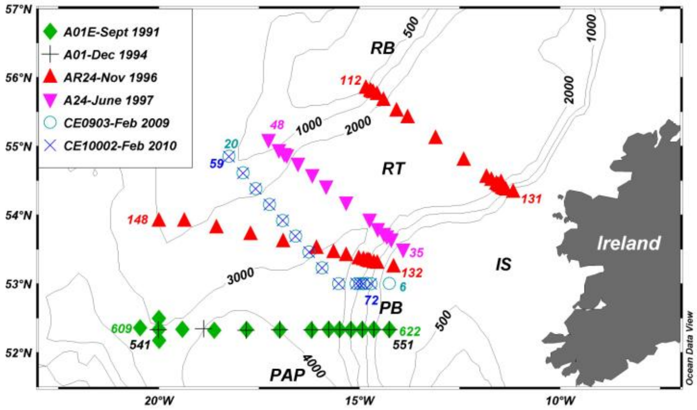

Figure 1. Bathymetry of the Rockall Trough. Labelled bathymetry: RT-Rockall Trough; IS-Irish Shelf; PB-Porcupine Bank; RB- Rockall Bank; PAP-Porcupine Abyssal Plain; with overlying transect positions of WOCE A01E (Sept 1991), A01 (Dec 1994), AR24 (Nov 1996), A24 (June 1997), CE0903 (Feb 2009) and CE10002 (Feb 2010). Station numbers of the surveys are at the end of each transect.

Table 1. Information on surveys discussed in the paper with details on the chemistry data available. Data sources: WOCE-World Ocean Circulation Experiment (https://cdiac.ornl.gov/oceans/); NUIG-National University of Ireland, Galway; MI-Marine Institute, Ireland. Chemistry samples: C_T; dissolved inorganic carbon; A_T; total alkalinity; NUT; dissolved inorganic nutrients; O_2; dissolved oxygen. Note while there were A_T data taken in 1991 and 2009, there was a large offset in the data, and while there were no oxygen bottle samples taken in 2009, oxygen sensor data is available.

Survey	**Date**	**Source**	**C_T**	**A_T**	**NUT**	**O_2**
A01E	17-21 Sept 1991	WOCE	√	x	√	√
A01	13-15 Dec 1994	WOCE	√	x	√	√
AR24	22-27 Nov 1996	WOCE	√	√	√	√
A24	8-10 June 1997	WOCE	√	√	√	√
CE0903	6-10 Feb 2009	NUIG, MI	√	x	√	x
CE10002	11-14 Feb 2010	NUIG, MI	√	√	√	√

2.1 Ancillary data

Details of temperature, salinity and oxygen sensors used in the 2009 and 2010 surveys, along with sampling, analysis and quality control of dissolved inorganic nutrients and oxygen are supplied in McGrath et al. (2012). Details of WOCE survey methods can be found on the CDIAC website and in CDIAC (2003). It should be noted that there were no oxygen bottle samples analysed in 2009, and therefore the sensor data were calibrated based on the assumption that the surface mixed layer is 97% saturated in winter, as was measured in the 1994, 1996 and 2010 winter surveys. Since there was a variability of ±2% in the oxygen saturation in surface waters of these surveys, this increases the uncertainty of oxygen results from ±1.5µmol kg^{-1} in Winkler data to ±5.6µmol kg^{-1} in the 2009 sensor data.

2.2 Dissolved Inorganic Carbon (C_T) and Total Alkalinity (A_T)

2009 and 2010 C_T and A_T were sampled and analysed as per Dickson et al. (2007). C_T was analysed by coulometric titration and A_T by potentiometric titration (Dickson et al., 2007) at NUI, Galway, both on a VINDTA-3C (Versatile INstrument for the Determination of Total inorganic carbon and titration Alkalinity), manufactured by Marianda (Mintrop et al., 2000). The system was calibrated by running duplicate Certified Reference Materials with every batch of samples (CRMs provided by A. Dickson, Scripps Institute of Oceanography, USA). The precision of both CRMs and samples was calculated as the standard deviation of the difference between duplicate samples; precision was ±2µmol kg^{-1} for C_T and ±1µmol kg^{-1} for A_T. There appears to be a negative offset of 7-8µmol kg^{-1} down through the water column in the 2009 A_T data relative to all other data sets. If this uncorrected data was included in the study, the lower A_T would result in anthropogenic carbon estimates over 20% higher than those presented for the 19 years. Such a large difference in A_T between 2009 and the other datasets is unlikely; A_T can not be expected to vary that much through the entire water column in the open ocean, especially since the 2009 salinity is similar to the other surveys. The only process that could reduce A_T would be a large increase in $CaCO_3$ formation through the water column, which is very unlikely. At present the reason for the offset is unknown, and therefore the 2009 A_T data have not been included in the present study.

WOCE C_T samples were analysed by coulometric detection on the SOMMA system (Johnson et al., 1987) and precision was ±2µmol kg^{-1} for all surveys. WOCE AR24 and A24 A_T was determined by potentiometric titration on a MATS system (Millero et al., 1993); precision was ±1µmol kg^{-1}. While there is a small number of A_T samples in the Trough from A01E, results are at least 40µmol kg^{-1} higher than other datasets and have therefore not been included here. Wanninkhof et al. (2003) also found A01E A_T values significantly different from neighbouring cruises and recommended that it not be used. There are no A_T data from the 1994 A01 survey.

Where A_T data was not available (1991, 1994, 2009), a multiple linear regression (MLR) approach was applied to the available A_T datasets to derive an equation that could calculate A_T from temperature, salinity, C_T, phosphate and silicate. A separate MLR was derived for the depths above and below 2000m due to the large difference in A_T profiles. Details of the MLRs of the combined dataset of 1996, 1997 and 2010 surveys are in the SI. Residuals are normally distributed and centred at zero, and the r-squared of the calculated versus measured A_T is 0.91 in the top 2000m and 0.97 below 2000m. The uncertainty of the estimated A_T, calculated as the standard deviation of residuals, is ±3µmol kg^{-1}.

To investigate the vertical distribution of A_T in the water column without the effect of salinity, it was normalised to a salinity of 35 as described by Friis et al. (2003);

$$NA_T = (A_T^{meas} - A_T^{S=0})/S^{meas} \bullet S^{ref} + A_T^{S=0}$$

where NA_T is the normalised A_T, A_T^{meas} is the measured A_T, S^{meas} is the measured salinity of the sample and S^{ref} is 35. $A_T^{S=0}$ is the salinity adjustment based on the constant term of salinity = 0. Friis et al. (2003) calculated $A_T^{S=0}$ as 728.3µmol kg^{-1} from combined North Atlantic surface data, with an uncertainty for NA_T of ±7µmol kg^{-1}. Although this calculation is based on surface waters of the North Atlantic, we have applied it here to the entire water column to give a broad idea of the normalised A_T distribution. The exact NA_T values are therefore not discussed since the calculation does not apply to waters at depth or from waters originating outside of the North Atlantic.

2.3 Calculation of pH and aragonite/calcite saturation

pH and aragonite/calcite saturation were calculated from the C_T and A_T data (along with potential temperature, salinity, pressure, silicate and phosphate data) using CO2SYS (Lewis and Wallace, 1998). The total pH scale was used, K_1 and K_2 were taken from Mehrbach et al. (1973), refit by Dickson and Millero (1987) and Dickson's K_{HSO4} was selected. pH was also calculated at 25ºC to investigate temporal changes between 1991 and 2010 and to allow for comparison with trends already published at this temperature. Calculating the uncertainty of the derived parameters is complicated as it includes the measurement uncertainties of each input parameter, along with the error in the equilibrium constants. Dickson and Riley (1978) calculated a combined uncertainty of 0.6 – 6.3% in pH and of 3.1% for the carbonate ion concentration, when calculated from A_T and C_T. The highest possible uncertainty is used with the results in this paper.

2.4 Estimation of anthropogenic carbon (ΔC_{ant})

C_T was corrected for changes in remineralisation of organic matter and dissolution of calcium carbonate ($\Delta C_{T\text{-}abio}$) using the equation from Tanhua et al., (2006);

$$\Delta C_{T\text{-}abio} = \Delta C_T - 0.746 \times \Delta AOU - 0.5 \times (\Delta A_T + \Delta NO_3)$$

where Δ is the change in properties between the earlier WOCE surveys and the recent 2009/10 surveys, AOU is the apparent oxygen utilisation, 0.746 is the stoichiometric ratio relating inorganic carbon to oxygen, calculated for the Northeast Atlantic by Körtzinger et al. (2001) and 0.5 is the effect on C_T by change in A_T due to dissolution of calcium carbonate. The combined analytical uncertainty in determining $\Delta C_{T\text{-}abio}$ is estimated to be ±3µmol kg^{-1}, based on the 2010 dataset. When A_T is estimated from

MLR the uncertainty of $\Delta C_{T\text{-abio}}$ increases to ±4μmol kg^{-1}, and in 2009, when both A_T and O_2 are estimated it increases to ±5μmol kg^{-1}. Since $\Delta C_{T\text{-abio}}$ is independent of the effects of the biological pump, it can therefore be assumed that any changes in $\Delta C_{T\text{-abio}}$ within a water mass are due to increasing levels of anthropogenic CO_2.

The change in anthropogenic carbon between the 1991 and 2010 surveys was also calculated using extended Multiple Linear Regression, eMLR, as described by Friis et al. (2005) and Tanhua et al. (2007). Here, C_T was fit with an MLR as a function of common hydrochemical parameters that influence its distribution.

$$C_T = a_0 + a_1 \cdot p_1 + a_2 \cdot p_2, .., + a_n \cdot p_n + R$$

where p_1 to p_n are the set of parameters used in the regression, a_0 to a_n are the corresponding coefficients and R is the residual. Separate MLRs were used for the depth range 200-1000m and 1000-2200m due to different water masses present. The separate coefficients determined from the regressions of the 2 surveys (a_0 to a_n, and b_0 to b_n) are subtracted to create a new equation that relates only the temporal difference in C_T to the hydrochemical parameters. This is interpreted as the change in C_T due to increasing levels of anthropogenic CO_2, ΔC_{ant}^{eMLR} (Tanhua et al., 2007).

$$\Delta C_{ant}^{eMLR} = (a_0 - b_0) + (a_1 - b_1) \cdot p_1 + (a_2 - b_2) \cdot p_2, \ldots, (a_n - b_n) \cdot p_n + R$$

Details of the MLRs that were used to calculate ΔC_{ant}^{eMLR} are in Table 2. The eMLR was applied to the 1991 dataset as there were more data points and the residuals were closer to zero (Figure 2). The two main assumptions of the eMLR method are (1) that the linear multiple-parameter model is able to describe a regions spatially varying hydrographic C_T distribution and (2) that the underlying natural correlations of C_T with the selected independent parameters do not change over the period of interest. A number of studies have highlighted that natural variability in oceanic C_T can be comparable to or larger than the anthropogenic signal sought by the decadal repeat occupations due to the influence of ocean circulation on annual variations in C_T (Doney et al., 2009; Levine et al., 2008; Rodgers et al., 2009). This eMLR technique accounts for the natural variations of carbon due to both hydrographic (temperature and salinity) and biogeochemical (nutrients and oxygen) parameters incorporated into the model. It should therefore account for changes in water mass movement between the surveys.

It is difficult to directly assess the accuracy and precision of the eMLR based estimate of ΔC_{ant}, see Tanhua et al., (2007) and Wanninkhof et al. (2010) for a discussion on the robustness of the eMLR method. The independent variables in the eMLR are not fully uncorrelated which can potentially lead to biases in the method. Even though the eMLR technique tends to cancel out the residual in the individual MLRs, the residual of the MLR fit for the two cruises can give an idea of the uncertainty in the eMLR based ΔC_{ant} estimate (see Figure 2). Assuming that the residual of the individual MLRs are independent suggest that the precision of the eMLR is ±4μmol kg^{-1}, even though this does not account for potential biases in the eMLR approach.

Table 2. Derived multiple linear regression equations for C_T prediction of 1991 (WOCE-A01E) and 2010 (CE10002) for two separate depth intervals, with the average residual (R); the predicted C_T minus measured C_T, the regression coefficient (R^2) and the number of samples (n) for each regression.

		a_0	$a_1(\theta)$	$a_2(S)$	$a_3(O_2)$	$a_4(NO_3)$	$a_5(Si)$	R	R^2	n
200-1000m	1991	1427.62	-6.32	24.60	-0.47	0.09	1.59	-0.7	0.99	43
200-1000m	2010	2025	2.50	0.10	0.13	3.34	3.69	-0.6	0.96	27
1000-2200m	1991	4203.55	11.18	-61.25	-0.03	1.40	2.55	-0.3	0.98	27
1000-2200m	2010	3926.82	-13.33	-43.39	-1.05	6.35	-2.41	-1.0	0.87	13

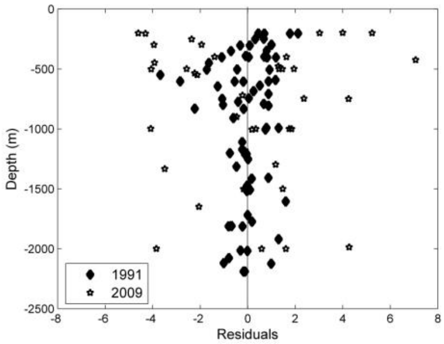

Figure 2. C_T MLR residuals (C_T predicted minus C_T measured) for both the 1991 and 2010 datasets.

3 Results and Discussion

3.1 Carbonate parameters of water masses in the Rockall Trough

3.1.1 Physical oceanography

A full description of the CE0903, CE10002 and AR24 temperature, salinity, oxygen and nutrient data is given in Mc Grath et al. (2012). Potential temperature-salinity plots and salinity sections for each of the surveys listed in Table 1 are in Fig. 1 and 2 of the Supplementary Information (SI). To summarize, ENAW (Eastern North Atlantic Water) as described by Harvey (1982), occupies much of the water column in the top 1000m in all surveys. As the relatively saline ENAW travels north from its formation region in the Bay of Biscay (Pollard et al., 1996), it is progressively freshened by mixing with water masses moving in from the west (Ellett et al., 1986). Between 500-1000m along the southern transects in the Rockall Trough, temperature and salinity tend towards MW (Mediterranean Water) on the eastern side of the Trough, while on the western side some of the data points tend towards SAIW (Sub Arctic Intermediate Water). SAIW forms in the western boundary current of the subpolar gyre; this cold, fresh water mass spreads westwards with a branch of the North Atlantic Current (NAC) to the southern entrance of the Trough (Arhan, 1990; Arhan et al., 1994; Harvey and Arhan, 1988). MW, also called Mediterranean Overflow Water (MOW), is a highly saline outflow from the Mediterranean Sea (Pérez et al., 1993; Tomczak and Godfrey, 1994) that is normally seen as an inflexion towards higher salinity in the θ-S (potential temperature-salinity) plots in the Rockall Channel (Ellett and Martin, 1973). The strength of these water mass signals varies between years; strongest MW signal is apparent in 1996, while strongest SAIW signal is apparent in 2010 (Fig. 1 in SI). While there is a weak inflexion towards MW signal in A24, the signal is less than that seen in other years, and is likely due to a more northerly position than the other southern Rockall transects.

θ-S profiles are similar across all years below 1500m, and indicate a clear LSW (Labrador Sea Water) signal between 1500-2000m deep. LSW is formed from deep winter convection in the Labrador Basin, and water properties of LSW can vary between years depending on local climate factors that influence the convection regimes in the Labrador Sea (Azetsu-Scott et al., 2005; Yashayaev, 2007). Northeast Atlantic Deep Water (NEADW) is seen as a salinity maximum about 2600m between the fresh LSW above it and LDW (Lower Deep Water) below it. (Ellett and Martin, 1973; van Aken, 2000), with some Antarctic Bottom Water (AABW) in the deepest parts of the Trough. AABW is formed by deep convection associated with the freezing of sea ice in the Weddell and Ross Seas, (Tomczak and Godfrey, 1994), it flows north along the eastern side of the North Atlantic and mixes up into NEADW, which then circulates into the Rockall Trough (Ellett and Martin, 1973; McCartney, 1992; New and Smythe-Wright, 2001; Tsuchiya et al., 1992).

For the AR24 northern transect, once again much of the top 1000m falls along the ENAW line. While there are no MW or SAIW signals apparent in this transect, there is a clear LSW signal, with LDW in the deepest parts of the transect. Due to the shallower depth of the northern transect, there is no AABW signal.

3.1.2 Vertical profiles

Vertical profiles of C_T broadly reflect the influence of the ‘biological pump’ in the ocean. C_T concentrations are lower in summer surveys than in winter and concentrations increase in all surveys below the surface mixed layer down to 1000m (Fig. 3a). Carbon is taken up in the surface ocean where organic matter and $CaCO_3$ are produced; this material is then transported to deeper waters where remineralisation releases inorganic carbon back into the water column. There is a slight decrease in C_T between 1500-2000m due to the presence of LSW, a relatively young water mass in the Northeast Atlantic (Yashayaev et al., 2007). Concentrations increase again to maximum levels in the deepest parts of the Trough due to high levels of remineralisation in the older NEADW and AABW. Apart from a few high-A_T points about 1000m (Fig. 3b), A_T profiles illustrate a steady decrease from surface waters down to a minimum between 1500-2000m, before gradually increasing towards a maximum in the deepest waters. A comparison of A_T with NA_T profiles (Fig. 3c) indicates that above 2000m, A_T is largely governed by salinity. Below 2000m the dissolution of $CaCO_3$ influences the A_T distribution since NA_T increases steadily to the deepest parts of the Trough. These profiles are similar to those measured off the Iberian Peninsula by Ríos et al. (1995), who found a sharp increase in A_T below 2300m due to the dissolution of $CaCO_3$. The high A_T signal (Fig. 3b) measured at ~1000m along the Irish shelf edge is due to the presence of MW, which is characteristically high in A_T due to high evaporation and hence salinity, coupled with high freshwater A_T inputs (Schneider et al., 2007).

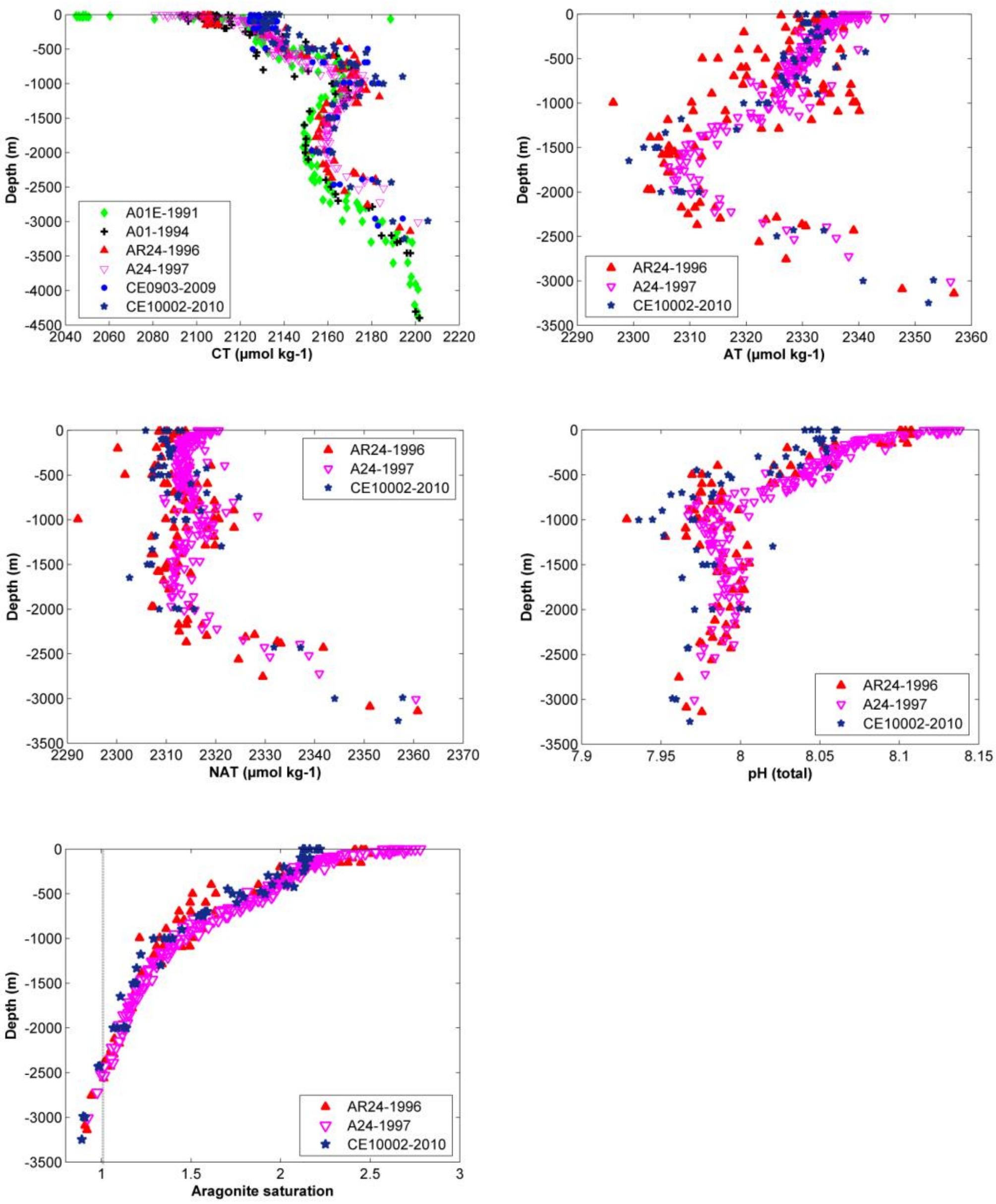

Figure 3. Vertical profiles of the carbonate parameters with depth (m) for A01E (Sept 1991), A01 (Dec 1991), AR24 (Nov 1996), A24 (June 1997), CE0903 (Feb 2009) and CE10002 (Feb 2010); (a) C_T (b) A_T (c) NA_T (d) pH (total scale) and (e) aragonite saturation, with the sample potential temperature as the reference temperature. Note the longer depth scale for C_T is due a greater depth in A01E and A01.

3.1.3 Surface mixed layer

The surface mixed layer is a region in the upper ocean where there is little variation in water properties with depth. Here we have defined the mixed layer depth (MLD) as the depth where the temperature is less than the surface value by 0.5°C (Monterey and Levitus, 1997). The average MLD for each survey is given in Table 3. To calculate the averages of water parameters within the mixed layer, the minimum MLD from each survey was used as the depth limit to ensure the given parameters are representative of the entire mixed layer across each transect.

The surface C_T across the various surveys highlights the effects of the biological and physical forcing on chemical parameters in the water column. Deepest MLDs were measured in 2009/10 surveys due to late-winter sampling, close to the end of winter mixing. Nutrient and C_T concentrations are higher than other surveys through regeneration from subsurface waters from deep vertical mixing. The average C_T concentration in the surface mixed layer of 2010 ($2133\pm2\mu$mol kg^{-1}) is similar to concentrations in the surface mixed layer along the western side of the Trough in 2009 ($2133\pm2\mu$mol kg^{-1}), and represent ENAW of western origin with slightly cooler temperatures, lower salinity and higher nutrients. Average C_T levels are slightly lower ($2128\pm2\mu$mol kg^{-1}) in the top 200m at stations closer to the shelf in 2009 relative to the western side of the Trough, coinciding with higher temperature and salinity and lower nutrients (Fig. 4, Table 3). This east-west gradient was also seen in the surface layer of the June 1997 survey and in both cases is likely related to the pathway of ENAW from the Bay of Biscay. Upwelling in the subpolar gyre regenerates surface waters with nutrients and C_T from below the permanent thermocline (Williams and Follows, 2003) which are mixed from the west across the Rockall Trough. Lower C_T ($2105\pm2\mu$mol kg^{-1}) in the Dec 1994 and Nov 1996 surveys coincides with a slightly shallower mixed layer and lower nutrient concentrations. This is largely due to sampling in early winter where mixing had not fully replenished C_T and nutrients to surface waters in the Trough. The average mixed layer depth is slightly deeper in the northern transect of AR24 (224m) relative to the southern transect (180m), and coincides with elevated nutrient and C_T concentrations due to increased mixing in the surface layer moving north in the Trough.

In A01E (Sept 1991) and A24 (June, 1997), higher surface temperature and a seasonal thermocline less than 45m deep, are both typical N. Atlantic features during the summer months. Results from the June survey indicate the progression of the spring-summer bloom as the water column stratifies, and photosynthesis in the surface waters results in a decrease in nutrients and C_T, with negative AOU values as oxygen is produced in the process. In September 1991, nutrients are almost depleted, with lowest surface nutrient and C_T values, likely marking the end of the spring-summer bloom (Table 3). Elevated A_T in the surface waters during the June and September surveys relative to the winter surveys, is likely related to photosynthesis in surface waters, which slightly increases A_T due to the uptake of protons with nitrate by phytoplankton (Millero et al., 1998b; Wolf-Gladrow et al., 2007).

3.1.4 Intermediate Waters (500-1100m)

The east-west gradient in carbonate parameters across the southern entrance to the Trough observed between 500-1100m is likely due to the pathway of ENAW and also the presence of SAIW and MW, two water masses with differing chemical properties. Highest levels of A_T at these intermediate depths were generally found at stations close to the shelf, coinciding with higher salinities (Fig. 3) and low oxygen, particularly seen in AR24. For example in AR24 average A_T was 2335±1μmol kg^{-1} (2333-2338μmol kg^{-1}) near the continental shelf (stations 137-139), while it averaged 2316±1μmol kg^{-1} (2296-2331μmol kg^{-1}) further west in the Trough (station 144-146). This gradient was not observed in the NA_T data and is therefore related to salinity distribution. The high A_T along the shelf edge must therefore be related to the more saline ENAW in the upper 1000m along the eastern side of the Trough, and also due to the presence of MW between 700-1000m, a highly saline core, characteristically low in oxygen and high in A_T (Cabecadas et al., 2002; Howe et al., 1974; Santana-Casiano et al., 2002). Like oxygen, A_T can therefore be used as an effective tracer of MW in the Rockall Trough. There is also an east-west gradient in C_T between 500-1100m, particularly seen in AR24 and CE0903 (Fig. 4). For example in CE0903 the average C_T between 500-1100m is 2155±2μmol kg^{-1} (2126-2183μmol kg^{-1}) at stations 7-13 near the shelf, while the average is 2171±2μmol kg^{-1} (2153-2180 μmol kg^{-1}) at stations 15-19 at the western side of the Trough. Like in surface waters, the gradient in C_T and nutrients is likely related to water from the subpolar gyre which has been subjected to high levels of winter mixing and upwelling (Pelegrí et al., 2006; Williams and Follows, 2003). Upwelling transports nutrient- and carbon-rich deeper waters back up the water column. In 2010, the higher C_T from the western side of the Trough was measured all the way across the intermediate depths (average C_T

2168±2µmol kg^{-1}) and is likely related to an elevated SAIW influence that year (McGrath et al., 2012). SAIW likely acquired its high C_T signal from mixing and upwelling in the subpolar gyre when it was formed, and due to low temperatures in its formation region which increases the capability of absorbing more CO_2. The east-west gradient in water parameters is less marked in the northern transect of AR24 relative to the southern transect, due to increased mixing and the absence of SAIW and MW signals.

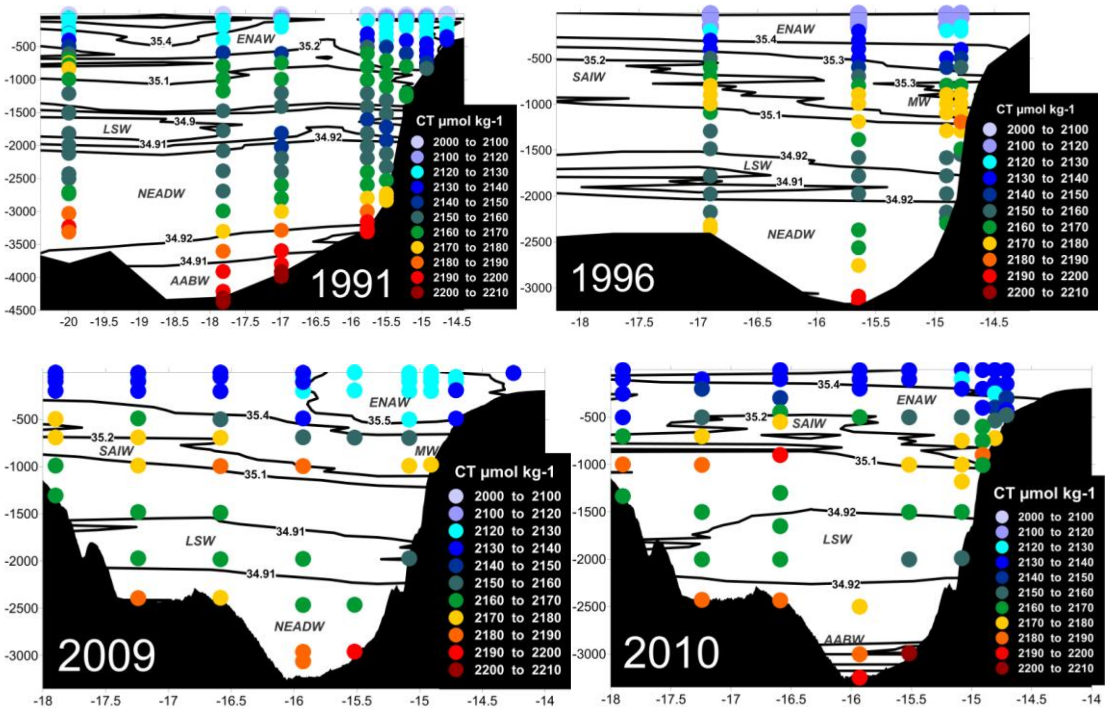

Figure 4. Section profiles of C_T (µmol kg^{-1}) with salinity contours and water masses across the southern Rockall Trough in 1991, 1996, 2009 and 2010.

3.1.5 Deep waters (>1500m)

There is a strong LSW signal both in the northern and southern transects of the Trough, with characteristically low salinity and high oxygen concentrations. The isopycnals used to describe LSW in a number of studies range between 27.68-27.80 kg m^{-3} (Dengler et al., 2006; Kieke et al., 2006), however this range would suggest that LSW occupies between 900-2500m deep in the Trough. We have however looked at the core of LSW at depths between 1500-2000m, which each year has an average density of 27.75-27.76 kg m^{-3} (ranging between 27.71-27.80 kg m^{-3}), and coincides with the characteristic salinity minimum and oxygen maximum values.

In the vertical profiles (Fig. 3a), there is a clear decrease in C_T between 1500-2000m in all datasets relative to the rest of the water column which coincides with the relatively young age of LSW in the Trough, as inferred from CFC data (not shown). The minimum A_T measured at this depth range is due to the low salinity of LSW; as it is absent in the NA_T profiles. Average A_T ranges from 2305-2309µmol kg^{-1} in LSW in all datasets, similar to A_T values reported for LSW near the Iberian Peninsula by Pérez et al. (1993). Below LSW there is a slight increase in salinity, and decrease in temperature, typical of NEADW. Within this water mass, oxygen concentrations decrease downwards, with a steady increase in nutrients and C_T below 2000m due to remineralisation of organic matter (Fig. 4a). There is also a steady increase in both A_T and NA_T from below 2000m to the deepest parts of the Trough due to the dissolution of $CaCO_3$ (Fig. 3b and 3c). Traces of AABW were found in the deepest water (>3000m) at the southern entrance to the Rockall Trough, identified using silicate data (McGrath et al., 2012). Highest concentrations of C_T and A_T (and NA_T) are also found at these depths; however there are too few data points to accurately describe the carbonate characteristics of this water mass in the Trough.

3.2 Temporal trends in carbonate parameters between 1991 and 2010

The effects of increasing atmospheric CO_2 on surface water pH can only be compared over the winter months, when biological activity is at a minimum. It is not possible to investigate the change in anthropogenic carbon signal in the surface waters of the Trough due to varying times of sampling between surveys. The WOCE winter surveys were completed in early winter and therefore inorganic carbonate parameters had not reached preformed conditions like in 2009 and 2010. Data from the Mace Head Atmospheric Research Station along the west coast of Ireland show an increase in pCO_2 from 355.4ppm at the end of winter in 1991 to 393.5ppm at the end of winter in 2010 (Michele Ramonet, personal communication). Assuming that the air-sea disequilibrium of CO_2 remained constant, along with constant salinity, temperature and alkalinity, this increase of 38.1ppm pCO_2 is equivalent to an increase in C_T of

18μmol kg^{-1} and a reduction in pH of 0.038 units (calculated using CO2SYS; Lewis and Wallace, 1998) in surface waters of the Trough over the 19 years.

Sub-surface water, i.e. water at the bottom of the mixed layer in winter surveys and below the thermocline in summer surveys, nutrient and carbon concentrations were examined to identify changes in the 'preformed' carbon conditions between all surveys, without direct seasonal influences (Table 4). Due to varying nutrient and AOU concentrations between the surveys, direct comparisons of C_T and subsequent pH can not differentiate between anthropogenic and natural factors affecting the C_T distribution. After correcting C_T for remineralisation and dissolution of calcium carbonate, the increase in $C_{T\text{-abio}}$ is 18±3μmol kg^{-1} in the subsurface layer between 1991 and 2010 (Fig. 5). This is insignificantly less than the increase of 19±4μmol kg^{-1} in the calculated ΔC_{ant}^{eMLR} in subsurface waters over the same period. Both estimates suggest an increase in ΔC_{ant} of ~1μmol kg^{-1}yr^{-1} in the Trough between 1991 and 2010. Direct comparison of calculated pH at these depths indicates that pH in subsurface waters has decreased by 0.055±0.004 units since 1991; however the increase in C_T of 25±2μmol kg^{-1} may be in part due to the higher AOU and nutrient levels, and hence biological activity, in 2010 relative to 1991. Therefore, 18μmol kg^{-1} and 19μmol kg^{-1} C_T was added to the 1991 dataset to investigate the change in pH due to the $\Delta C_{T\text{-abio}}$ and ΔC_{ant}^{eMLR}. The increase in $C_{T\text{-abio}}$ is equivalent to a decrease in pH of 0.039±0.002, while the increase in C_{ant}^{eMLR} is equivalent to a pH reduction of 0.041±0.003. Both indicate that subsurface waters in the Trough have acidified by ~0.020 pH units per decade. This is in line with observations from a number of time series (Hawaii Ocean Time-series, the Bermuda Atlantic Time-Series Study, and European Station for Time-Series in the Ocean in the eastern Atlantic) who measured a decrease of 0.02 pH units per decade over the last 20 years (IPCC, 2007). Results are also supported by atmospheric CO_2 data from Mace Head which indicated a reduction in pH in surface waters of 0.02 pH units per decade, assuming constant air-sea disequilibrium. Finally, while surface and subsurface waters are still supersaturated with respect to aragonite and calcite, there is a gradual decrease in saturation states between 1991 and 2010, with a reduction in aragonite saturation from 2.17±0.07 to 1.88 ±0.06, and a reduction in calcite saturation from 3.40±0.11 to 2.94±0.09, in subsurface waters over the 19 years. Recent field and laboratory experiments have found that despite carbonate saturation greater than 1

Table 3. Average concentration of the chemical parameters of the surface mixed layer from A01E, A01, AR24, A24, CE0903 and CE10002. Standard deviations are in *italics* beside the average concentrations. MLD; average mixed layer depth across the transects and *n*; number of carbon samples from each survey. pH (total), aragonite (ArΩ) and calcite (CaΩ) saturation were calculated using CO2SYS, details described in Methods section. pH was calculated at potential temperature (θ). The * indicates where A_T or O_2 are estimated.

Year	MLD	Depth	ST	S	T	DO	AOU	NO_3	Si	PO_4	C_T	A_T	pH (t) T=θ	ArΩ	CaΩ	n
Sept 1991	51	0-40	all	35.32 (0.09)	15.41 (0.47)	246.3 (3.0)	-1.3 (1.5)	0.45 (0.30)	0.68 (0.15)	0.15 (0.03)	2049 (4)	2337*(6)	8.161*(0.004)	3.11*(0.06)	4.83*(0.09)	12
Dec 1994	211	0-135	all	35.45 (0.08)	11.31 (0.25)	256.7 (2.3)	9.4 (1.4)	8.38 (0.70)	2.50 (0.29)	0.54 (0.03)	2106 (6)	2334*(5)	8.108*(0.008)	2.44*(0.04)	3.81*(0.07)	29
Nov 1996	180	0-135	132-148	35.45 (0.07)	11.40 (0.17)	258.8 (1.6)	6.9 (1.3)	7.08 (0.33)	2.29 (0.29)	0.52 (0.02)	2105 (1)	2332 (3)	8.105 (0.003)	2.44 (0.03)	3.82 (0.05)	12
			112-131	35.40 (0.10)	10.96 (0.25)	259.8 (1.7)	8.5 (0.8)	7.82 (0.33)	2.81 (0.23)	0.55 (0.02)	2115 (8)	2329 (3)	8.087 (0.017)	2.31 (0.08)	3.62 (0.13)	11
June 1997	45	0-25	35-41	35.47 (0.05)	12.73 (0.56)	269.9 (1.6)	-12.4 (1.6)	4.27 (0.56)	0.48 (0.07)	0.30 (0.03)	2088 (5)	2339 (1)	8.128 (0.008)	2.71 (0.05)	4.23 (0.08)	7
		0-25	42-47	35.46 (0.04)	11.97 (0.32)	270.1 (4.0)	-7.6 (4.1)	5.41 (0.52)	1.00 (0.45)	0.37 (0.04)	2097 (4)	2339 (2)	8.127 (0.006)	2.61 (0.03)	4.08 (0.05)	7
Feb 2009	470	0-200	7-14	35.53 (0.01)	11.16 (0.06)	259.2*(0.5)	7.8*(0.6)	10.03 (0.38)	3.45 (0.11)	0.54 (0.04)	2128 (3)	2338*(0)	8.070*(0.008)	2.25*(0.05)	3.53*(0.07)	17
			15-20	35.45 (0.01)	10.56 (0.17)	259.0*(1.3)	11.3*(1.3)	11.44 (1.03)	4.38 (0.87)	0.66 (0.08)	2133 (3)	2333*(1)	8.059*(0.007)	2.16*(0.05)	3.38*(0.08)	11
Feb 2010	450	0-200	all	35.47 (0.04)	10.75 (0.27)	262.4 (2.9)	7.0 (1.9)	10.06 (0.44)	3.33 (0.24)	0.59 (0.05)	2133 (2)	2332 (2)	8.052 (0.007)	2.16 (0.04)	3.38 (0.06)	12

Table 4. Average concentration of the chemical parameters of the subsurface waters from A01E, A01, AR24, A24, CE0903 and CE10002. Standard deviations are in *italics* beside the average concentrations and *n* is the number of carbon samples from each survey. pH (total), aragonite (ArΩ) and calcite (CaΩ) saturation were calculated using CO2SYS, details described in Methods section. pH was calculated at both potential temperature (θ) and 25ºC. The * indicates where A_T or O_2 are estimated.

Year	Depth	S	T	DO	AOU	NO_3	Si	PO_4	C_T	A_T	pH (t) T=θ	pH (t) T=25ºC	$C_{T\text{-abio}}$	ArΩ	CaΩ	n
1991	150-250	35.44 _(0.08)_	10.56 _(0.57)_	248.0 _(3.3)_	22.9 _(1.5)_	11.74 _(0.56)_	4.99 _(0.45)_	0.77 _(0.05)_	2125 _(2)_	2337*_(3)_	8.077*_(0.004)_	7.861*_(0.009)_	934*_(2)_	2.21*_(0.05)_	3.47*_(0.08)_	11
1994	200-300	35.43 _(0.07)_	10.52 _(0.59)_	246.9 _(3.4)_	23.7 _(4.5)_	12.16 _(1.17)_	4.37 _(0.68)_	0.74 _(0.06)_	2125 _(7)_	2333*_(3)_	8.072*_(0.012)_	7.855*_(0.017)_	935*_(5)_	2.17*_(0.09)_	3.40*_(0.13)_	11
1996	200-300	35.42 _(0.07)_	10.51 _(0.47)_	242.3 _(2.7)_	28.1 _(3.4)_	11.82 _(0.71)_	4.96 _(0.50)_	0.77 _(0.05)_	2132 _(5)_	2329 _(7)_	8.047 _(0.013)_	7.832 _(0.015)_	941 _(6)_	2.06 _(0.07)_	3.23 _(0.11)_	4
1997	150-250	35.43 _(0.03)_	10.31 _(0.26)_	255.7 _(4.2)_	16.0 _(4.5)_	10.95 _(0.70)_	4.79 _(0.62)_	0.72 _(0.04)_	2129 _(4)_	2334 _(2)_	8.069 _(0.009)_	7.850 _(0.010)_	945 _(3)_	2.15 _(0.05)_	3.38 _(0.08)_	16
2009	400-500	35.42 _(0.13)_	10.36 _(0.97)_	242.0*_(19.4)_	30.8*_(27.0)_	12.15 _(3.04)_	4.97_(2.36)_	0.70 _(0.22)_	2149 _(21)_	2332*_(6)_	8.020*_(0.042)_	7.798*_(0.057)_	949*_(3)_	1.88*_(0.24)_	2.94*_(0.36)_	6
2010	400-500	35.42 _(0.11)_	10.32 _(0.70)_	235.4 _(17.7)_	35.8 _(20.5)_	13.80 _(2.96)_	5.61_(1.86)_	0.82 _(0.18)_	2150 _(11)_	2332 _(5)_	8.014 _(0.029)_	7.797 _(0.030)_	952 _(6)_	1.88 _(0.14)_	2.94 _(0.21)_	8

Table 5. Average concentration of the chemical parameters in Labrador Sea Water between 1500-2000m across the southern Rockall Trough from A01E, A01, AR24, A24, CE0903 and CE10002. Standard deviations are in *italics* beside the average concentrations and *n* is the number of carbon samples from each survey. pH (total), aragonite (ArΩ) and calcite (CaΩ) saturation were calculated using CO2SYS, details described in Methods section. pH was calculated at both potential temperature (θ) and 25ºC. The * indicates where A_T or O_2 are estimated.

Year	**S**	**T**	**DO**	**AOU**	**NO_3**	**Si**	**PO_4**	**C_T**	**A_T**	**pH (t) T=θ**	**pH (t) T=25ºC**	**$C_{T\text{-abio}}$**	**ArΩ**	**CaΩ**	**n**
1991	**34.90** *(0.01)*	**3.59** *(0.10)*	**277.1 *** *(2.1)*	**41.4** *(1.8)*	**17.17** *(0.23)*	**11.62** *(0.57)*	**1.17** *(0.01)*	**2150** *(1)*	**2306*** *(1)*	**8.014*** *(0.004)*	**7.697*** *(0.004)*	**958*** *(2)*	**1.21*** *(0.03)*	**1.87*** *(0.05)*	**11**
1994	**34.91** *(0.02)*	**3.76** *(0.34)*	**270.8** *(8.5)*	**46.0** *(5.7)*	**18.21** *(0.39)*	**10.93** *(0.51)*	**1.16** *(0.02)*	**2151** *(4)*	**2306*** *(2)*	**8.008*** *(0.010)*	**7.691*** *(0.005)*	**955*** *(3)*	**1.19*** *(0.06)*	**1.84*** *(0.03)*	**5**
1996	**34.92** *(0.02)*	**3.69** *(0.27)*	**272.2** *(4.9)*	**45.6** *(3.3)*	**17.4** *(0.19)*	**12.01** *(0.73)*	**1.16** *(0.01)*	**2156** *(2)*	**2306** *(3)*	**7.996** *(0.007)*	**7.680** *(0.005)*	**961** *(2)*	**1.16** *(0.04)*	**1.80** *(0.06)*	**14**
1997	**34.93** *(0.01)*	**3.72** *(0.23)*	**267.4** *(5.5)*	**49.3** *(4.8)*	**17.33** *(0.11)*	**13.03** *(0.83)*	**1.16** *(0.01)*	**2160** *(2)*	**2309** *(2)*	**7.995** *(0.006)*	**7.680** *(0.009)*	**961** *(2)*	**1.17** *(0.04)*	**1.82** *(0.06)*	**18**
2009	**34.91** *(0.01)*	**3.65** *(0.21)*	**267.8*** *(6.7)*	**46.4*** *(2.3)*	**17.53** *(0.69)*	**11.49** *(0.98)*	**1.09** *(0.08)*	**2160** *(4)*	**2307*** *(1)*	**7.989*** *(0.015)*	**7.671*** *(0.013)*	**962*** *(5)*	**1.10*** *(0.03)*	**1.70*** *(0.05)*	**5**
2010	**34.92** *(0.01)*	**3.67** *(0.20)*	**273.3** *(4.3)*	**44.0** *(2.1)*	**18.00** *(0.65)*	**11.97** *(1.26)*	**1.09** *(0.03)*	**2160** *(3)*	**2305** *(4)*	**7.985** *(0.014)*	**7.669** *(0.012)*	**966** *(4)*	**1.13** *(0.05)*	**1.76** *(0.08)*	**9**

(supersaturated), a decrease in saturation state resulted in a decrease in calcification rate of most calcifying organisms (Feely et al., 2004; Veron et al., 2009, and references within).

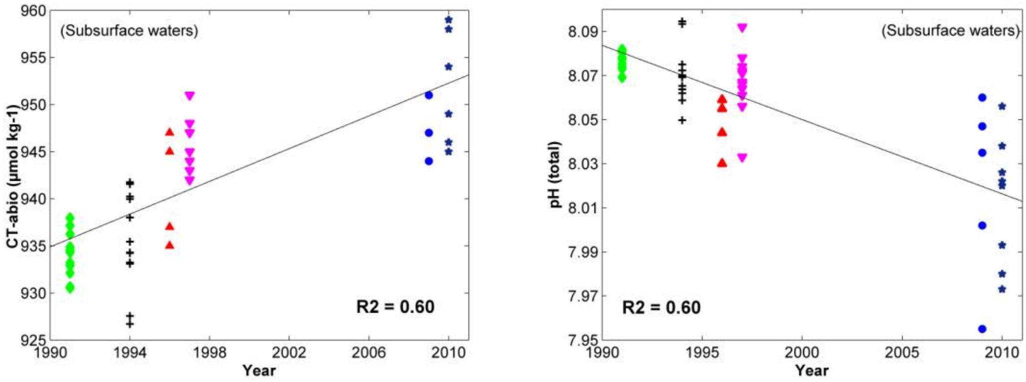

Figure 5. (a) $\Delta C_{T\text{-abio}}$ concentration (µmol kg^{-1}) and (b) pH (total scale, calculated using in situ C_T, A_T, θ, salinity, pressure, Si and PO_4) in the subsurface waters across all transects of the southern Rockall Trough between 1991 and 2010.

At intermediate depths (500-1100m), it is difficult to directly compare the inorganic carbonate parameters due to varying thermohaline profiles and water mass signals between surveys. Despite the large range in inorganic carbon, the span in C_T each year did progressively increase from 2133-2172µmol kg^{-1} in 1991 to 2151-2194µmol kg^{-1} in 2010, and a comparison of the upper and lower pH limits indicates a decrease in pH of 0.026 – 0.043 ±0.003 units over the 19 years. The increase in C_{ant}^{eMLR} over the same period averaged 15±4µmol kg^{-1}, ranging from 8 to 22µmol kg^{-1} between 500-1000m. The increasing C_T and decreasing pH observed in both the subsurface and intermediate depths may therefore have implications for the cold water corals living in the Trough, which are found mainly between 500-1000m deep (White and Dorschel, 2010).

While there is no overall trend in nutrient concentrations, C_T levels increased from 2150 to 2160µmol kg^{-1} in LSW between 1991 and 2010 (Table 5). Out of this increase of 10µmol kg^{-1} C_T, 8µmol kg^{-1} can be attributed to anthropogenic carbon signal since both $\Delta C_{T\text{-abio}}$ and ΔC_{ant}^{eMLR} estimated an increase of 8±4µmol kg^{-1} in LSW between 1991 and 2010 (Fig. 6). This indicates an increase in anthropogenic carbon of 0.4µmol $kg^{-1}yr^{-1}$ in LSW in the Trough. Due to changing convection regimes in the Labrador Sea, the air saturation of LSW may vary and rates between 70-100% have been reported (Azetsu-Scott et al., 2005). While $\Delta C_{T\text{-abio}}$ is affected by time-varying

CO_2 air-sea disequilibrium due to the assumption of constant air saturation during formation, the eMLR method should incorporate such effects through the use of salinity and potential temperature in the regression. Pérez et al. (2010) measured a similar increase in C_{ant} of ~9µmol kg^{-1} in LSW in the eastern North Atlantic between 1981 and 2006.

There is a decrease in the calculated pH in this water mass of 0.029±0.002 pH units (at in situ temperature) and 0.027±0.002 at 25ºC over the 19 years (Fig. 6, Table 5). Regardless of the initial saturation state or temperature used to calculate pH, there has been a reduction in pH in LSW in the Trough at a rate of 0.015 units per decade. LSW in the Rockall Trough is still supersaturated with calcite and aragonite, with a slight decrease in both aragonite (0.08±0.01) and calcite (0.11±0.01) saturation between 1991 and 2010 (Table 5). Due to the gradual increase in C_T in LSW, without corresponding increase in nutrients or AOU, we assume that this increase in $C_{T\text{-abio}}$ and C_{ant}^{eMLR}, and decrease in pH, is due to increasing levels of anthropogenic carbon in its source water in the Labrador Sea. The rate of increase in C_T in LSW is slower than the observed increase in subsurface waters in the Trough. This may be because surface waters in the Labrador Sea cannot keep pace with increasing atmospheric $p\text{CO}_2$ due to fast transport times away from the surface during deep convection (Tanhua et al., 2007; Terenzi et al., 2007). Also, LSW has not been subjected to as high atmospheric $p\text{CO}_2$ as the subsurface waters that were more recently in contact with the atmosphere. See section of ΔC_{ant}^{eMLR} at the southern entrance to Rockall between 1991 and 2010 (Fig. 7).

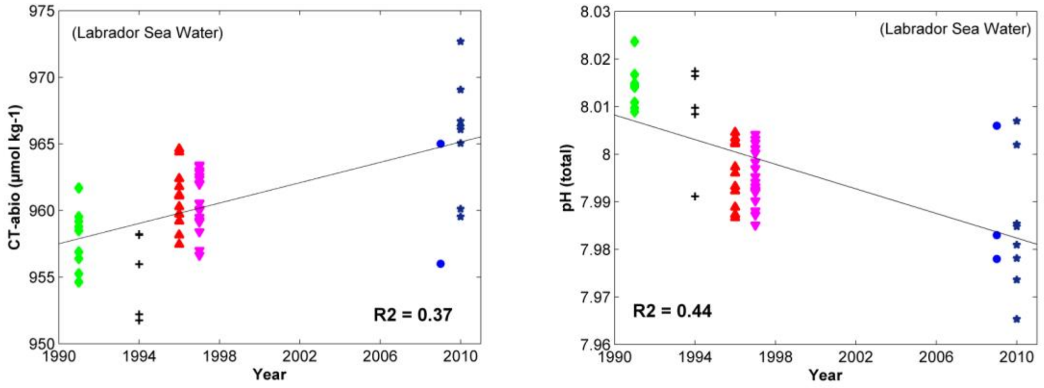

Figure 6. (a) $\Delta C_{T\text{-abio}}$ concentration (µmol kg^{-1}) (b) pH (total scale, calculated using in situ C_T, A_T, θ, salinity, pressure, Si and PO_4) between 1500-2000m across all transects of the southern Rockall Trough between 1991 and 2010.

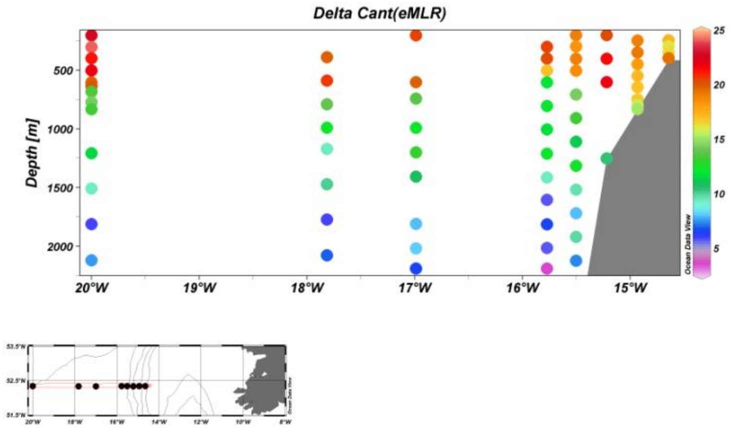

Figure 7. ΔC_{ant}^{eMLR} (μmol kg^{-1}) between 200-2200m across the southern Rockall Trough between 1991 and 2010.

In upper NEADW, between 2000 and 2500m deep, there is an increasing trend in C_T ($R^2 = 0.61$) over the 19 years, ranging from 2150-2161µmol kg^{-1} in 1991 to 2170-2189µmol kg^{-1} in 2010. There is a reduction in calculated pH of 0.029±0.002 between 1991 and 2009/10 ($R^2 = 0.68$) in this depth range and an increase in $C_{T\text{-abio}}$ of 3±3µmol kg^{-1}. The increasing maximum value of C_T in NEADW may indicate that we are seeing the effects of increasing atmospheric CO_2 at depths >2000m in the Trough. This is supported by Pérez et al. (2010) who measured an increase in C_{ant} of 4µmol kg^{-1} in the NADWu (upper North Atlantic Deep Water) between 1981 and 2006 off the Iberian Peninsula.

Between 2500-3000m, C_T also gradually increases ($R^2 = 0.45$), ranging from 2158-2185µmol kg^{-1} in 1991 to 2182-2206µmol kg^{-1} in 2010, with a subsequent decrease in pH of 0.019 ($R^2 = 0.47$). $\Delta C_{T\text{-abio}}$ however only increases 2±3µmol kg^{-1} over the 19 years. Due to only a few data points in the 2009/10 surveys below 2000m, ΔC_{ant}^{eMLR} could not be calculated. Unfortunately we cannot draw conclusions on the changing saturation horizon in the Trough due to a small number of data points below 2300m in 2009/10. We do however expect a decrease in the depth of aragonite saturation horizon (ASH) in the North Atlantic due to increasing anthropogenic CO_2 penetration. There has already been a 20% reduction in calcium carbonate saturation between 1766 and 2007 (Caldeira and Wickett, 2003; Gattuso and Lavigne, 2009). In the eastern North Atlantic the ASH has shoaled by ~400m since the Industrial Revolution and is projected to decrease by ~700m by 2050 (Tanhua et al., 2007). It is expected that the Arctic will be undersaturated with respect to aragonite within a decade

(Steinacher et al., 2009). The ASH in the nearby Iceland Sea is shoaling at a rate of 4m yr^{-1} (Olafsson et al., 2009).

C_T ranges between 2180-2205µmol kg^{-1} across all surveys below 3000m, however there is only 1 data point in 2009 and 1 in 2010, so we cannot draw conclusions about decadal changes in carbonate chemistry in AABW between surveys. Pérez et al. (2010) reported C_{ant} in lower NADW off the Iberian Peninsula between 4-9µmol kg^{-1}, with no overall increasing/decreasing trend between 1981 and 2006. It is expected that AABW should have only a small anthropogenic signal due to its high age.

The storage of anthropogenic carbon between 1991 and 2010 was calculated by integrating the vertical profiles of ΔC_{ant}^{eMLR}. We provide an estimate of the carbon storage rate between 1991 and 2010 of 0.70±0.08 mol m^{-2} yr^{-1} between 200-1000m, and 0.50±0.04 mol m^{-2} yr^{-1} between 1000-2000m. If we assume a constant air-sea CO_2 disequilibrium, the storage rate for the top 200m is 0.17±0.01 mol m^{-2} yr^{-1}, resulting in a total storage rate for the upper 2000m in the Trough of 1.37±0.13 mol m^{-2} yr^{-1}. The higher storage rates of the upper water column are likely associated with the warmer, saltier waters of the eastern North Atlantic with a large buffer capacity (Sabine and Tanhua, 2010).

4. Conclusion

We have described a comprehensive dataset of inorganic carbon and associated parameters from a range of water masses in the Rockall Trough, against which future changes can be measured. The 2009 and 2010 datasets provide a baseline of late winter or ‘preformed’ inorganic carbon and acidity levels in the surface waters of the Trough. Comparisons with data from WOCE surveys in the 1990’s show that the pH in subsurface waters in the Trough has decreased by 0.040±0.003 units due to a gradual increase in $C_{T\text{-}abio}$ and C_{ant}^{eMLR} of 18 – 19 ±4µmol kg^{-1} between 1991 and 2010. This is in line with a number of other time series who also measured a decrease in pH of 0.02 units per decade. It appears that rising C_T in subsurface waters in the Trough is keeping pace with changes in atmospheric CO_2 concentrations since the increase in pCO_2 measured at Mace Head is equivalent to a similar increase in C_T and decrease in pH. ΔC_{ant} has increased in LSW by 8±4µmol kg^{-1}, with a reduction in pH of 0.029±0.002 over the 19 years. There has been a gradual reduction in aragonite and calcite saturation states which may have implications for calcifying organisms in the region, particularly the cold water corals along the Irish continental shelf. The total water column storage rate of 1.37±0.13 mol m^{-2} yr^{-1} is significantly larger than the global average of 0.55 mol m^{-2} yr^{-1} (Sabine et al., 2008). In general we think that this observed increase in anthropogenic carbon is robust as two independent methods for calculating ΔC_{ant} give consistent results and show high level of agreement with other studies in the North Atlantic.

Acknowledgements

This study was funded by the Irish Government funded project "Impacts of Increased Atmospheric CO_2 on Ocean Chemistry and Ecosystems", with Colin O'Dowd as PI and carried out under the Sea Change strategy with the support of the Marine Institute and the Marine Research Sub-Programme of the National Development Plan 2007-2013. Surveys were funded by the Irish government's National Development Plan 2007-2013. We are grateful to the officers, crew and scientists on the cruises referred to in this paper. We thank Kieran Lyons and Glenn Nolan for their help in Matlab, and Jonathan White for his help with R. We would like to extend our gratitude to two anonymous reviewers for their constructive and careful comments.

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Supplementary Information
Inorganic carbon and pH levels in the Rockall Trough
McGrath, T., Kivimae, C., Tanhua, T., Cave, R.R., McGovern, E.

Potential Temperature-Salinity Plots

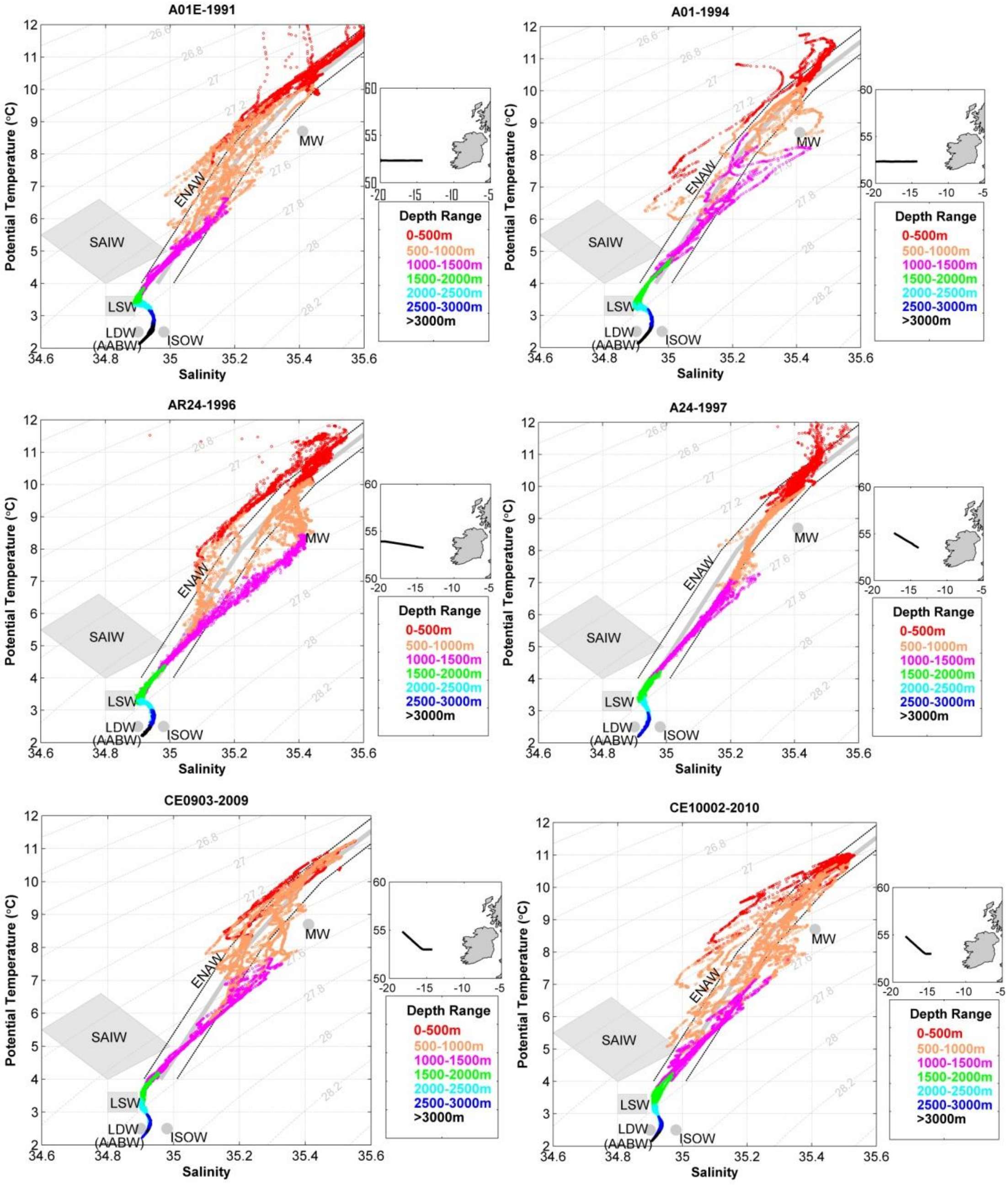

Figure 1. θ-S plots with density contours, using CTD data of the southern transect from (i) A01E, (ii) A01 (iii) AR24, (iv) A24, (v) CE0903 and (vi) CE10002. A subplot outlining the transect position is beside each θ-S plot. Water mass properties were taken from the literature: ENAW, MW, LSW and AABW (Harvey, 1982); SAIW (Bubnov, 1968; Harvey and Arhan, 1988); LDW (Holliday et al., 2000); ISOW

(Harvey, 1982; van Aken and Becker, 1996). Note the temperature and salinity of MW is much higher in the source region, properties plotted here are typical of MW in the eastern North Atlantic.

Salinity contour sections

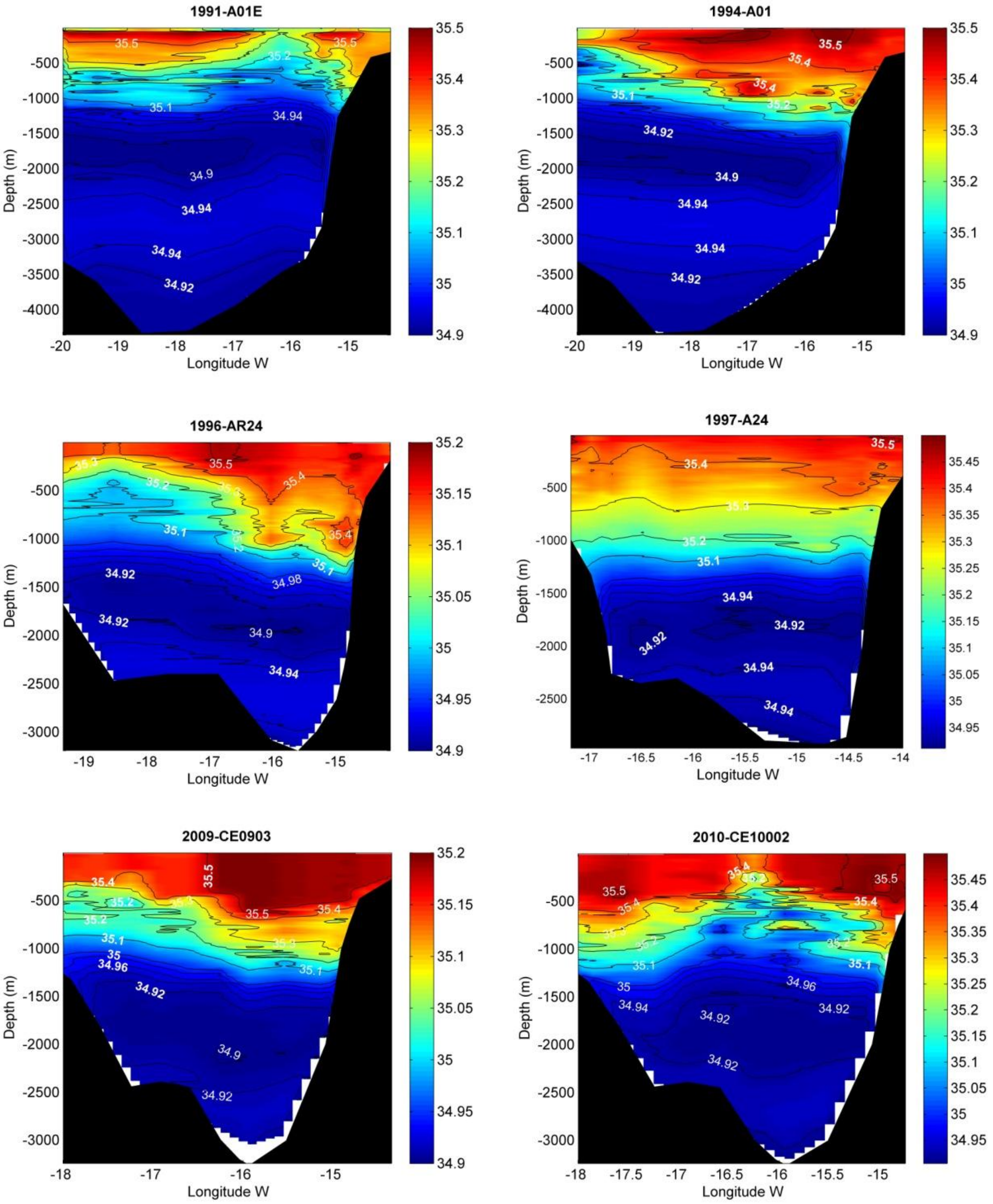

Figure 2. Salinity contour sections across the Rockall Trough for each of the surveys.

Calculation of A_T using multiple linear regression, where A_T is a function of temperature, salinity, C_T, PO_4 and Si.

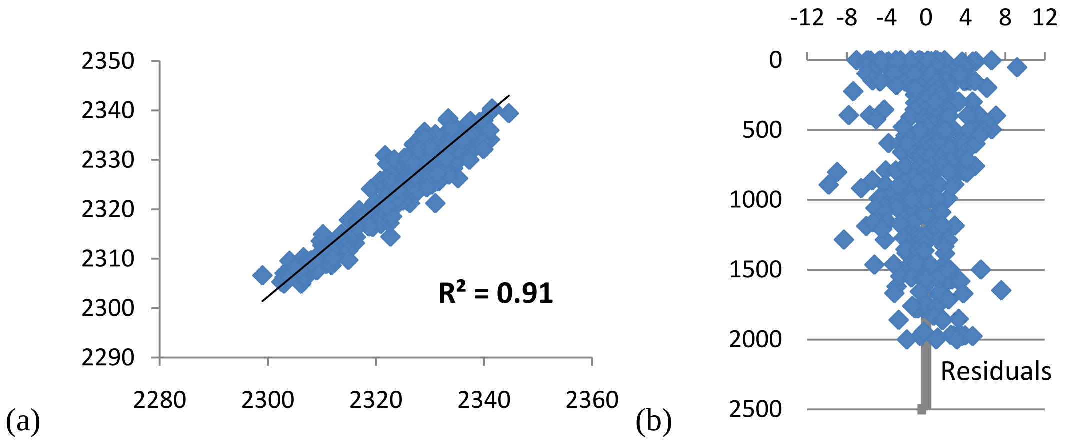

Figure 2. (a) Measured A_T plotted against the calculated A_T using multiple linear regression (MLR) in the top 2000m. (b) The residuals, measured A_T minus the calculated A_T, with depth (m).

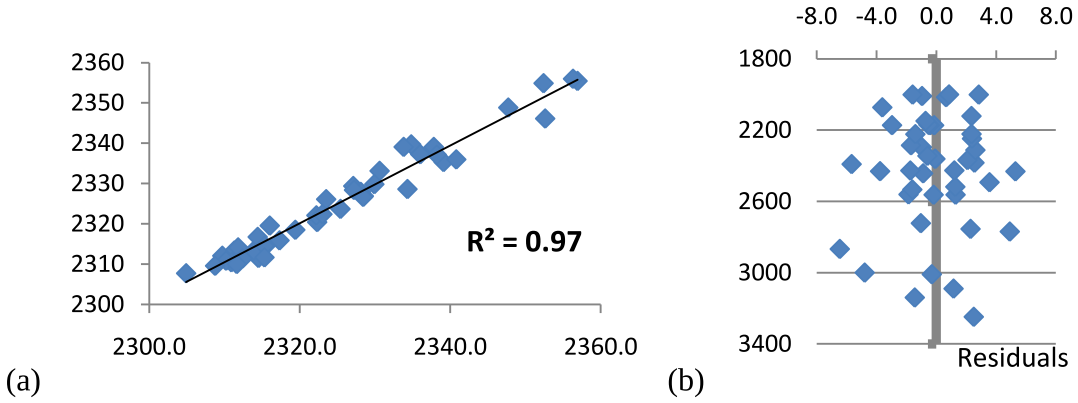

Figure 3. (a) Measured A_T plotted against the calculated A_T using multiple linear regression (MLR) below 2000m. (b) The residuals, measured A_T minus the calculated A_T, with depth (m).

Table 1. Derived multiple linear regression equation for A_T prediction of the combined 1996, 1997 and 2010 datasets for the top 2000m and below 2000m; a_0 is the intercept, R is the average residual (the predicted A_T minus measured A_T), R^2 is the regression coefficient and *n* is the number of samples in the regression.

	a_0	a_1(T)	a_2(S)	a_3(C_T)	a_4(PO_4)	a_5(Si)	R	R^2	*n*
< 2000m	721.15	1.61	50.07	-0.09	-2.74	1.89	0	0.91	382
> 2000m	2124.82	7.79	10.33	-0.10	-10.54	2.15	-0.1	0.97	50

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