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**Rate of Iceland Sea  
acidification from  
time series  
measurements**

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# Rate of Iceland Sea acidification from time series measurements

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## Abstract

The Iceland Sea is one part of the Nordic Seas. Cold Arctic Water prevails there and the deep water is an important source of North Atlantic Deep Water. We have evaluated time series observations of measured  $p\text{CO}_2$  and total  $\text{CO}_2$  concentration from discrete seawater samples during 1985–2008 for changes in response to increasing atmospheric carbon dioxide. The surface pH in winter decreases  $0.0024\text{ yr}^{-1}$ , which is 50% faster than those at two subtropical time series stations, BATS and ESTOC. In the deep water regime ( $>1500\text{ m}$ ), the rate of pH decline is  $1/4$  of that observed in surface waters. The surface calcium carbonate saturation states ( $\Omega$ ) are about 1.5 for aragonite and 2.5 for calcite, and are about  $1/2$  those for subtropical waters. During the period 1985–2008, the degree of saturation ( $\Omega$ ) decreased at a rate of  $0.0072\text{ yr}^{-1}$  for aragonite and  $0.012\text{ yr}^{-1}$  for calcite. The aragonite saturation horizon is currently at  $1750\text{ m}$  and rising at  $4\text{ m yr}^{-1}$ . Based on local hypsography, each year causes  $800\text{ km}^2$  of sea floor, previously bathed in saturated waters, to be exposed to undersaturation conditions.

## 1 Introduction

The Nordic Seas lie north of the Greenland-Iceland-Faroes-Scotland Ridge, from which flows dense, cold overflow water to the North Atlantic (Hansen et al., 2008). The overflow waters are an important source for the global thermohaline circulation. The Iceland Sea is a constituent of the Nordic Seas. It is north of Iceland and divided by the Kolbeinsey Ridge, into two basins the western part being shallower (Fig. 1) (Jakobsson et al., 2008). The seafloor areas, depth and volumes, or hypsography, of the Nordic Seas has recently been described by Jakobsson (2002).

The hydrographic properties of the Iceland Sea can in essence be described as Arctic Intermediate Waters overlying Arctic Deep Water (Swift et al., 1980; Stefánsson, 1962). A time series of surface carbon chemistry observations was initiated in 1983 and

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includes temperature, salinity,  $p\text{CO}_2$  and the concentrations of total  $\text{CO}_2$  and macro-nutrients (Takahashi et al., 1985), Here we describe 21 years of winter-month observations made during 1985–2008. The time series station is at  $68.0^\circ\text{N}$ ,  $12.67^\circ\text{W}$  and has a bottom depth of 1850 m (Fig. 1). In mid-winter, temperature and salinity profiles

generally display gentle variations with depth, with smooth transitions from intermediate to deep water (Fig. 2). These observations provide a basis for evaluating the carbon chemistry changes that result from shifts in chemical equilibria as the level of atmospheric  $\text{CO}_2$  rises due to anthropogenic emissions.

There is increasing concern about the consequences of ocean acidification from the  $\text{CO}_2$  driven shifts in ocean carbon system chemical equilibria driving trends toward lower pH and  $\text{CaCO}_3$  saturation states, e.g. Royal Society (2005). Reactions involve firstly the hydrolysis of dissolved  $\text{CO}_2$ , which increases the  $\text{H}^+$  concentration and thus lowers pH:



Secondly  $\text{H}^+$  titrates the seawater carbonate and converts it to bicarbonate:



As the carbonate ion concentration is lowered, the solubility of calcium carbonate,  $\text{CaCO}_3$ , increases:



The solubility product for calcium carbonate is written as

$$K_{\text{sp}} = [\text{Ca}^{2+}]_{\text{sat}} [\text{CO}_3^{2-}]_{\text{sat}} \quad (\text{R4})$$

when water is in saturated with a calcium carbonate mineral, and the saturation state of calcium carbonate is

$$\Omega = [\text{Ca}^{2+}]_{\text{sw}} [\text{CO}_3^{2-}]_{\text{sw}} / K_{\text{sp}} = [\text{CO}_3^{2-}]_{\text{sw}} / [\text{CO}_3^{2-}]_{\text{sat}} \quad \text{where } [\text{Ca}^{2+}]_{\text{sw}} = [\text{Ca}^{2+}]_{\text{sat}} \quad (\text{R5})$$

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where the subscripts “sw” and “sat” refer to the concentration in seawater and at saturation. When  $\Omega$  is  $>1.0$  seawater is supersaturated, when  $\Omega$  is  $<1$  seawater is undersaturated. As the solubility of the different mineral phases of  $\text{CaCO}_3$  differ, so does  $\Omega$ . The solubility is higher for aragonite than for calcite. Consequently aragonite forming organisms are considered more sensitive to the decrease in  $[\text{CO}_3^{2-}]$  resulting from the additions of anthropogenic  $\text{CO}_2$  (Kleypas et al., 2006).

The effect of increasing  $\text{CO}_2$  and decreasing pH in seawater on the corresponding  $\Omega$  distribution field in the oceans has been observed by Feely et al. (2004). Substantial impact is anticipated in high-latitude oceans by late this century as assessed by Orr et al. (2005) using ocean-carbon models. Recently another ocean-carbon-climate model study has indicated that the largest pH changes in this century would be seen in the surface waters of the Arctic Ocean. Concurrently, aragonite undersaturation might occur locally and become widespread as atmospheric  $\text{CO}_2$  increases to more than 450 ppm (Steinacher et al., 2008). Observations show that currently the aragonite saturation horizon in the deep Arctic Ocean is at about 2500 m (Jutterström and Anderson, 2005). In this paper, we will focus on the Iceland Sea, southern part of the Nordic Seas, and assess the rate of surface and deep-water acidification from time series measurements.

## 2 Methods

### 2.1 Interpretation framework

For documenting long-term changes in the ocean chemistry, one needs a precise analytical method accompanied by well defined and stable standards for instrument calibration. Although direct measurements of pH or  $\text{H}^+$  ion concentration in seawater are desirable, commonly used electrode methods suffer from ambiguities in regards to whether measurements represent  $\text{H}^+$  ion activities, concentrations, or the sum of concentrations of  $\text{H}^+$  species involved in acid-base reactions. Additionally, intercomparison

of measurements made using different electrode systems is difficult because electrode liquid-junction potentials vary among calibration solutions, such as those used for the NBS scale (Bates, 1973) and those used for seawater (Bates and Culberson, 1977). Another parameter, total (or titration) alkalinity, may be determined precisely and reproducibly using calibrated HCl solutions. However, alkalinity is a statement of the neutrality of ionic charges, and consists of contributions from various acids including carbonic, boric, silicic, phosphoric and some organic acids. In principle, exact computation of pH using the alkalinity requires a precise understanding of these component acids, including their concentrations and dissociation constants. However, the concentrations of the nutrient salts are generally low in the northern waters, and hence neglecting the contributions of phosphoric and silicic acids from alkalinity introduces only small systematic errors in computed chemical parameters. A typical winter surface water in the Iceland Sea has the following properties; SST =  $-0.19^{\circ}\text{C}$ , salinity = 34.7, total alkalinity =  $2285\ \mu\text{eq/kg}$ ,  $\text{TCO}_2 = 2150\ \mu\text{mol/kg}$  with about  $4\ \mu\text{mol/kg}$  for silicate and  $0.7\ \mu\text{mol/kg}$  for phosphate. If silicate and phosphate are neglected, the resulting properties in seawater would yield the  $p\text{CO}_2$  value too low by  $2\ \mu\text{atm}$ , pH value too high by 0.002, and  $\Omega$  value too high by 0.01. Therefore, systematic errors introduced by neglecting them are within the experimental errors for the alkalinity ( $\pm 3\ \mu\text{eq/kg}$ ) and  $\text{TCO}_2$  ( $\pm 2\ \mu\text{mol/kg}$ ). On the other hand, in high nutrient waters such as those found in the Southern Ocean (silicate  $> 100\ \mu\text{mol/kg}$ ), the systematic errors may be as large as  $-10\ \mu\text{atm}$  in  $p\text{CO}_2$ ,  $+0.01$  in pH and  $+0.05$  in  $\Omega$ .

## 2.2 Data processing

In our study, we chose to measure  $p\text{CO}_2$  and  $\text{TCO}_2$  ( $=[\text{CO}_2]_{\text{aq}} + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ ). This method has two advantages. First, both the  $p\text{CO}_2$  and  $\text{TCO}_2$  are measured using common standards, that are calibrated using the volumetric  $\text{CO}_2$  method maintained earlier by the late C. D. Keeling and presently by P. Tans of ESRL, US NOAA. Second, using these two properties, pH and  $[\text{CO}_3^{2-}]$  in seawater may be computed using a set of  $\text{CO}_2$  solubility and the first and second apparent dissociation constants for carbonic

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acid in seawater without the concentrations and dissociation constants of other acid species such as boric, phosphoric, silicic acids. The precision of our  $p\text{CO}_2$  and  $\text{TCO}_2$  measurements is  $\pm 3 \mu\text{atm}$  and  $\pm 2 \mu\text{mol/kg}$  respectively. Accordingly, if the dissociation constants and solubility of  $\text{CaCO}_3$  are assumed to be known exactly, the precisions for the computed quantities should be  $\pm 1 \mu\text{mol/kg}$  for  $[\text{CO}_3^{2-}]$ ,  $\pm 0.004$  for pH and  $\pm 0.02$  for  $\Omega$ . However,  $\pm 5\%$  uncertainties in the dissociation constants for carbonic acid would cause an uncertainty of  $\pm 5 \mu\text{mol/kg}$  in  $[\text{CO}_3^{2-}]$  and  $\pm 0.02$  in pH. Furthermore,  $\pm 10\%$  uncertainty in the solubility of  $\text{CaCO}_3$  results in  $\pm 0.25$  uncertainty in  $\Omega$ . Therefore, when the values reported in this paper are compared with results obtained using other sets of dissociation constants, these levels of uncertainty must be taken into consideration.

We determined the partial pressure of carbon dioxide ( $p\text{CO}_2$ ) in discrete sea water samples using a gas chromatograph for gas samples equilibrated at  $4.0^\circ\text{C}$ , and total dissolved inorganic carbon ( $\text{TCO}_2$ ) using coulometry (Chipman et al., 1993). The  $p\text{CO}_2$  results were corrected to in situ temperatures using the temperature coefficient of  $0.0423^\circ\text{C}^{-1}$  (Takahashi et al., 1993). Accuracy of the  $\text{TCO}_2$  determinations is maintained since 1992 by comparison of results with reference material calibrated by Andrew G. Dickson of the Scripps Institution of Oceanography using C. D. Keeling's manometric system. From the observed  $p\text{CO}_2$  and  $\text{TCO}_2$  results we calculate pH (total pH scale) and calcium carbonate saturation using the CO2SYS software (Lewis and Wallace, 1998), in which the solubility of  $\text{CO}_2$  in seawater by Weiss (1974) and the apparent dissociation constants for carbonic acid of Mehrbach et al. (1973), as refit by Dickson and Millero (1987), are used. The CO2SYS also calculates aragonite and calcite solubility,  $K_{\text{sp}}$ , (Mucci, 1983) with pressure corrections.

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## 3 Results

### 3.1 Surface changes

There is large seasonality in the high-latitude North Atlantic both in physical and biogeochemical parameters (Takahashi et al., 1993). In high winter, daytime is short and convective cooling of the surface layer intense. The biological processes are at their seasonal minimum. However, the winter mixed layer depth extends generally only to about 200 m at the Iceland Sea time series station (Ólafsson, 2003). For the evaluation of long-term surface variations, we use only winter observations in upper 20 m, which were collected in the first 67 days of the year (25 January to 7 March) in order to minimize the biochemical effects.

Over the 23 year period of the surface-water time series, 1985–2008, the computed pH values reveal a strong decreasing trend (Fig. 3a). Taking into account the effect of interannual variability of surface layer temperature, a linear regression shows the rate of pH decline  $-0.0024 \text{ yr}^{-1}$  and an increase in  $[\text{H}^+]$  of about 14% over the 23 year period (Table 1 part A). The observed rate of pH decline is slower,  $-0.0017 \text{ yr}^{-1}$ , and the corresponding  $[\text{H}^+]$  increase smaller, 9%, at two subtropical Atlantic time series stations BATS near Bermuda (Bates, 2007) and ESTOC near the Canary Islands (Santana-Casiano et al., 2007). However, our rates are not directly comparable with those from BATS, which are based on season-detrended whole-year data, nor with ESTOC which is based on a multivariate regression on a whole-year data. The temperature effect  $0.0056^\circ\text{C}^{-1}$  computed from regression analysis (Table 1 part A) is larger than expected from the hydrographic temperature trend which suggests that it includes variations in other parameters, e.g.  $\text{TCO}_2$ , which influence pH. Addition of  $\text{TCO}_2$  to the multivariate regression would reduce the temperature coefficient to  $0.0045^\circ\text{C}^{-1}$  and change the pH change rate to  $-0.0022 \text{ yr}^{-1}$ .

In this cold water with a mean temperature of  $-0.3^\circ\text{C}$ , the saturation states,  $\Omega_{\text{ar}}$  and  $\Omega_{\text{ca}}$ , are low, and they have decreased over the observation period (Fig. 3b and Table 1 part A). The rates of  $\Omega$  change with time are comparable with those observed

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at BATS (Bates, 2007). The  $\Omega_{ca}$  is decreasing at a rate about 1.6 times faster than that of  $\Omega_{ar}$ ,  $-0.0117/-0.00721$  (Table 1). Since  $\Omega$  is inversely proportional to  $K_{sp}$  (Eq. 5), the rate of change in  $\Omega$  reflects the  $K_{sp}$  of these minerals: for a given change in  $[\text{CO}_3^{2-}]$  resulting from a pH change,  $\Omega(\text{calcite})/\Omega(\text{aragonite})=K_{sp}(\text{aragonite})/K_{sp}(\text{calcite})=1.6$ .

### 3.2 Deep water changes

We evaluate the changes in carbonate chemistry of deeper water from deep observations where seasonal variability is negligible. It is evident from the water column investigations 1994–2008 (Fig. 4) that pH and the carbonate saturation states of aragonite and calcite are decreasing, the isolines are shoaling with time. Over the duration of the observations the aragonite saturation horizon,  $\Omega_{ar}=1$ , shoals from 1763 m to 1710 m. For the deepest water the rate of change with time in the carbonate system parameters was evaluated from 97 samples from the 1500–1850 m depth range. As the solubility of calcium carbonate is pressure dependent, pressure and time are chosen as variables in a multivariate linear regression (Table 1 part B). The pressure (or depth) effects thus obtained are compared with the chemical equilibrium calculations using the pressure effect on  $K_{sp}$  of  $-\Delta V(\text{cm}^3)=36.00-0.20 \times (T^\circ\text{C})$  for calcite and  $=33.3-0.22 \times (T^\circ\text{C})$  for aragonite (Mucci, 1983). The equilibrium calculations indicate pressure effects of  $-5.0 \times 10^{-5} \text{ db}^{-1}$  for pH,  $-3.4 \times 10^{-4} \text{ db}^{-1}$  for  $\Omega_{ca}$  and  $-2.0 \times 10^{-4} \text{ db}^{-1}$  for  $\Omega_{ar}$ . The results of the multivariate linear regression would include the effects of pressure as well as other changes such as chemical compositions. Nevertheless, considering the uncertainties (up to 20% in  $\Delta V$ ; Broecker and Takahashi, 1976) in the pressure effect on the  $K_{sp}$  of calcite and aragonite, these results are mutually consistent, thus giving credence to our results.

In this near bottom layer, the pH is falling  $0.0006 \text{ yr}^{-1}$  (Table 1 part B) about 4 times slower than at the surface (Table 1 part A). The corresponding increase in  $\text{H}^+$  concentration over 23 years is 3.1% or about 1/4 of the surface rate of  $\text{H}^+$  increase.

Similarly, below 1500 m depth the aragonite saturation state is changing  $-0.0009 \text{ unit yr}^{-1}$  and the saturation horizon is shoaling with time (Table 1 part B).

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This rate of decline for  $\Omega_{ar}$  is 13% of that at the surface. The same applies to the  $\Omega_{ca}$  decline. The rate of shoaling of the aragonite saturation horizon (where  $\Omega_{ar}=1$ ) was evaluated using the regression coefficients in Table 1 part B and solving the multivariate linear regression for pressure when  $\Omega_{ar}=1$  and year=1995 and 2005. Over this 10-year period, the aragonite saturation horizon shoals by 37.8 m ( $4 \text{ m yr}^{-1}$ ). Thus substantial sea-floor area may undergo a transition from supersaturated to undersaturated conditions as determined by the hypsometry of the Iceland Sea, the shape of the basin as described by the relation between depth and sea-floor area.

The Iceland Sea is relatively shallow, the mean depth being 1026 m, whereas the mean depths of the adjacent Norwegian and Greenland Seas are, respectively, 1816 m and 1580 m (Fig. 1) (Jakobsson, 2002). The Iceland Sea aragonite saturation horizon,  $\Omega=1$ , is about 800 m shallower than in the Arctic where it is at about 2500 m (Jutterström and Anderson, 2005). The hypsometric curve for the Iceland Sea reveals a rather gentle slope in the depth range 1000–1800 m, such that a 1-m depth change corresponds to  $200 \text{ km}^2$  of sea floor (Fig. 5). As the aragonite saturation horizon is currently rising at  $4 \text{ m yr}^{-1}$ , each year  $800 \text{ km}^2$  of the Iceland Sea floor along with associated biota become exposed to waters that have just become undersaturated with respect to aragonite. This analysis assumes similar temperature, salinity and carbon chemistry properties within this depth range across the basin. Our data from both east of, and west of the Kolbeinsey Ridge, the latter being shallower, demonstrate that this assumption is valid (Table 2).

There are two major reasons why these changes in the Nordic Seas are faster than those in the subtropical Atlantic. First, the buffer capacity of the cold Arctic waters is less than that of subtropical waters. The Revelle factor in the Iceland Sea surface water in winter was about 15.2 in the early 2000 whereas in subtropical Atlantic waters at BATS it was then 9.2 (N. Bates, personal communication, 2009). Thus, for the same amount of  $\text{CO}_2$  added to seawater the reduction in pH would be more in the Iceland Sea surface water. Second, Iceland Sea surface waters are undersaturated with respect to atmospheric  $\text{CO}_2$  throughout the year due to low temperatures and intense

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biological utilization. Hence the Iceland Sea absorbs more CO<sub>2</sub> per unit area (Takahashi et al., 2002, 2009) as do the Nordic Seas in general (Skjelvan et al., 2005). The CO<sub>2</sub> air-sea flux has been estimated to be about 4.5 mol m<sup>2</sup> y<sup>-1</sup> (J. Olafsson, personal communication, 2009). Both the high air-sea CO<sub>2</sub> flux and the lower buffer capacity (higher Revelle factor) result in stronger acidification of Iceland Sea surface waters.

## 4 Conclusions

The anthropogenic increase of atmospheric carbon dioxide affects the Nordic Seas both at the surface and at depth. In the surface, the pH has decreased from 8.13 to 8.08 between 1985 and 2008, and the aragonite saturation ( $\Omega$ ), which is naturally low anyway, decreased from 1.6 to 1.5 between 1985 and 2008. In the deep water, the pressure effect adds to the low temperature, and above the depths of about 1500 m, the aragonite saturation horizon is shoaling at a rate of about 4 m yr<sup>-1</sup>. This shoaling results from extensive vertical mixing which transmits atmospheric signatures to waters as deep as 1500 m (Messias et al., 2008). Large areas of the benthos are thus undergoing a rapid transition from being exposed to waters that are supersaturated to being exposed to waters that are undersaturated with respect to aragonite. There is an urgent need to clarify the effects of these changes on associated benthic ecosystems, especially at shallower depths, where the population of carbonate forming benthic biota are much greater.

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**Table 1.** Multivariate regression coefficients with standard errors for  $y=ax+bz+c$  describing trends at the Iceland Sea time series station. Part A describes time trends, 1985–2008, and effects of temperature variations on surface pH and relative saturation stages of aragonite and calcite. Part B describes time trends, 1994–2008, and effects of pressure on pH and relative saturation stages of aragonite and calcite in the deepest water,  $p>1500$  db.

A				
<i>y</i>	<i>a</i> <i>x</i> =Time, year	<i>b</i> <i>z</i> =Temperature, <i>t</i> °C	<i>c</i> Constant	<i>r</i> <sup>2</sup>
pH	-0.0024±0.0002	0.00563±0.00270	13.00±0.38	0.907
Ω <sub>ar</sub>	-0.00721±0.00066	0.0778±0.0094	15.97±1.33	0.882
Ω <sub>ca</sub>	-0.0117±0.0011	0.121±0.015	25.78±2.13	0.882
B				
<i>y</i>	<i>a</i> <i>x</i> =Time, year	<i>b</i> <i>z</i> =Pressure, db	<i>c</i> Constant	<i>r</i> <sup>2</sup>
pH	-0.000601±0.000103	-0.000058±0.000004	9.318794±0.204435	0.767
Ω <sub>ar</sub>	-0.000948±0.000240	-0.000251±0.000009	3.332886±0.478023	0.906
Ω <sub>ca</sub>	-0.001508±0.000367	-0.000411±0.000013	5.288040±0.731239	0.916

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**Table 2.** Iceland Sea mean properties of the sea water in the depth range 1000–1500 db west and east of the Kolbeinsey Ridge.

	Pressure	$t^{\circ}\text{C}$	$S$	TIC $\mu\text{mol kg}^{-1}$	$p\text{CO}_2$ $\mu\text{atm}$	$\Omega_{\text{ar}}$	$\Omega_{\text{ca}}$	pH
Western basin	1135±142	-0.56±0.12	34.898±0.042	2161±4	329±15	1.18±0.06	1.86±0.10	8.052±0.019
Eastern basin	1207±164	-0.76±0.15	34.908±0.006	2166±5	330±4	1.17±0.05	1.83±0.08	8.049±0.009

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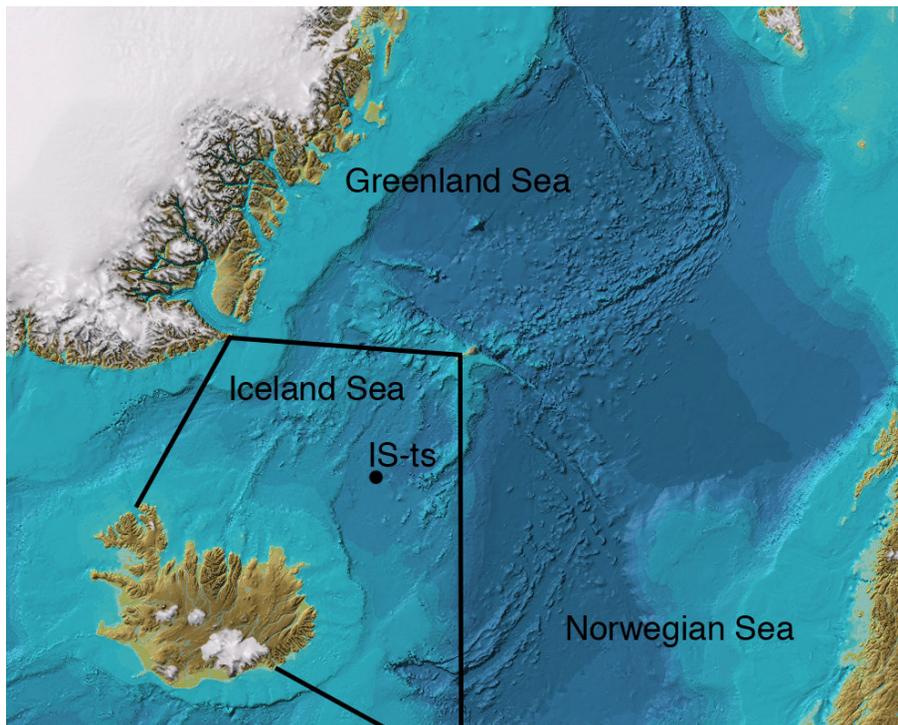
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**Fig. 1.** Portion of the IBCAO v.2 bathymetric chart (Jakobsson, 2008) showing the Iceland Sea time series station, IS-ts, and adjacent Nordic Seas. The Iceland Sea boundaries are based on Jakobsson (2002).

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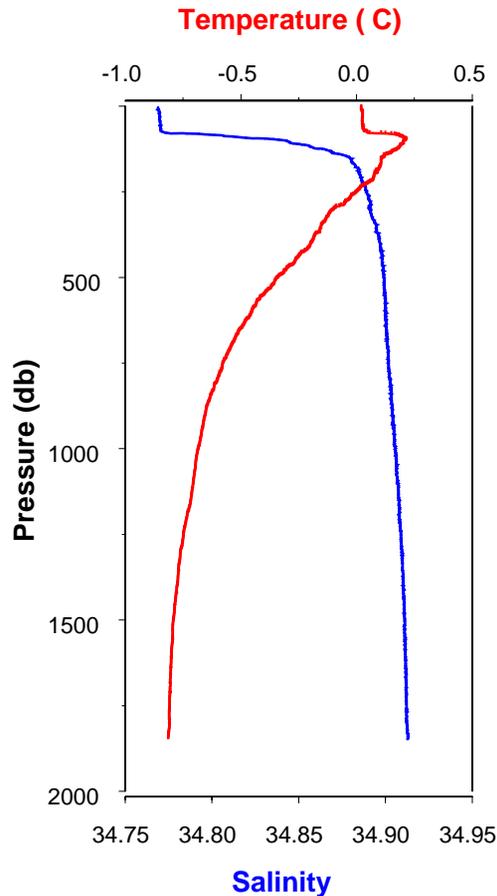
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**Fig. 2.** Winter 2006 profiles of temperature and salinity at the time series station, IS-ts, showing a 90 m seasonal mixed layer and homogenous water below 1500 m depth.

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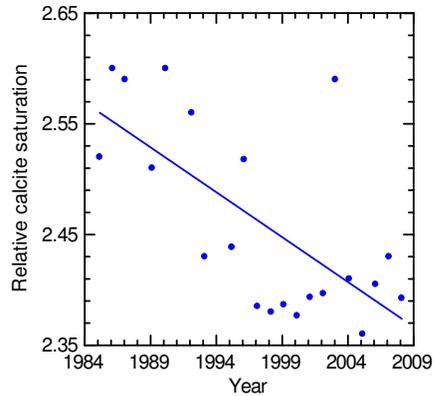
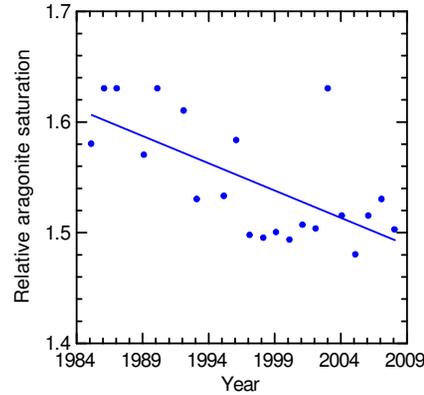
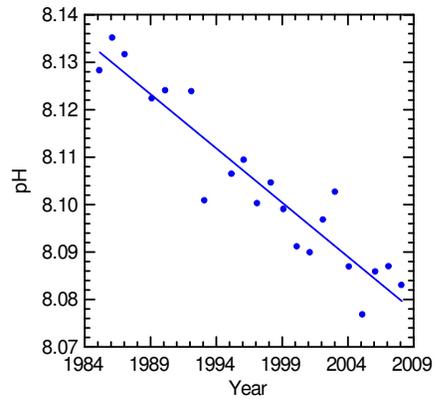
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**Fig. 3.** Iceland Sea winter surface water changes in pH, and the saturation state of aragonite and calcite ( $\Omega_{ar}$  and  $\Omega_{ca}$ ). Coefficients for the linear regression lines are shown in Table 1 part A.

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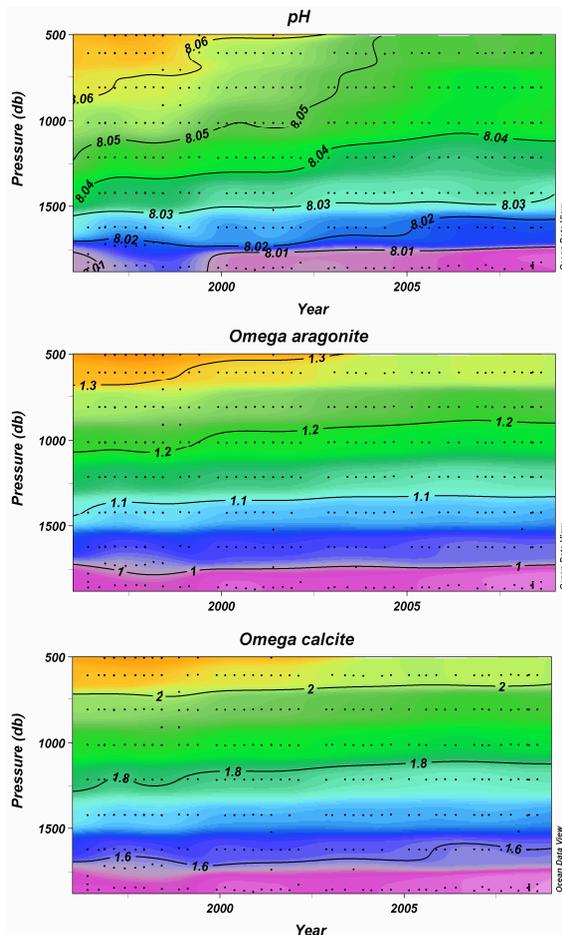


Fig. 4. Iceland Sea Time Series deep-water trends during 1994–2008 for pH, aragonite saturation and calcite saturation (Schlitzer, 2009). The station depth is 1850 m.

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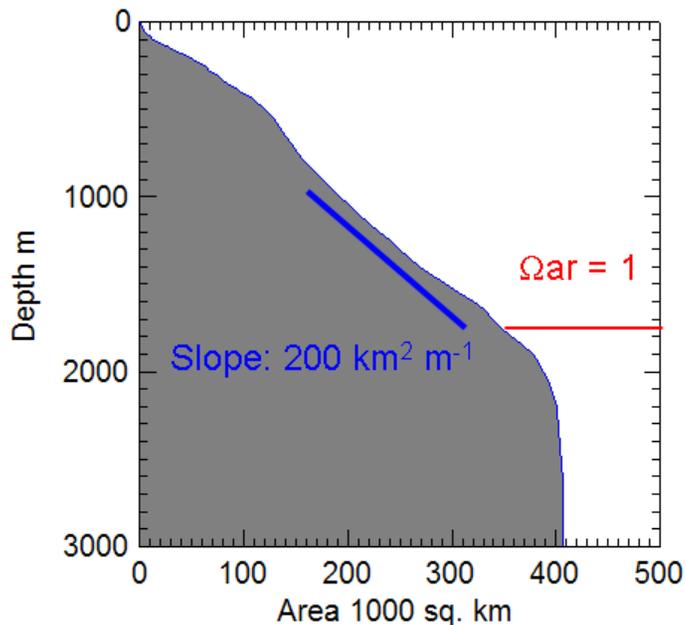
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**Fig. 5.** The hypsometry of the Iceland Sea (Jakobsson, 2002) shows that in the depth range 1000–1800 m, a 1 m shoaling of the aragonite saturation horizon results in  $200 \text{ km}^2$  of seafloor being exposed to bottom waters that are undersaturated with respect to aragonite.

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