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A Time-Series View of Changing Surface Ocean Chemistry Due to Ocean Uptake of Anthropogenic CO₂ and Ocean Acidification

BY NICHOLAS R. BATES, YRENE M. ASTOR, MATTHEW J. CHURCH, KIM CURRIE, JOHN E. DORE, MELCHOR GONZÁLEZ-DÁVILA, LAURA LORENZONI, FRANK MULLER-KARGER, JON OLAFSSON, AND J. MAGDALENA SANTANA-CASIANO

ABSTRACT. Sustained observations provide critically needed data and understanding not only about ocean warming and water cycle reorganization (e.g., salinity changes), ocean eutrophication, and ocean deoxygenation, but also about changes in ocean chemistry. As an example of changes in the global ocean carbon cycle, consistent changes in surface seawater CO₂-carbonate chemistry are documented by seven independent CO₂ time series that provide sustained ocean observations collected for periods from 15 to 30 years: (1) Iceland Sea, (2) Irminger Sea, (3) Bermuda Atlantic Time-series Study (BATS), (4) European Station for Time series in the Ocean at the Canary Islands (ESTOC), (5) CArbon Retention In A Colored Ocean sites in the North Atlantic (CARIACO), (6) Hawaii Ocean Time-series (HOT), and (7) Munida in the Pacific Ocean. These ocean time-series sites exhibit very consistent changes in surface ocean chemistry that reflect the impact of uptake of anthropogenic CO₂ and ocean acidification. The article discusses the long-term changes in dissolved inorganic carbon (DIC), salinity-normalized DIC, and surface seawater \( p_{\text{CO}_2} \) (partial pressure of CO₂) due to the uptake of anthropogenic CO₂ and its impact on the ocean’s buffering capacity. In addition, we evaluate changes in seawater chemistry that are due to ocean acidification and its impact on pH and saturation states for biogenic calcium carbonate minerals.
INTRODUCTION
Perturbation of the global carbon cycle through the production and release of anthropogenic carbon dioxide (CO$_2$) to the atmosphere has important implications for Earth’s climate (Solomon et al., 2007) and for ocean chemistry. In the atmosphere-terrestrial biosphere-ocean system, the marine carbon cycle is the largest active carbon reservoir on time scales relevant to human societies. Interacting physical and biogeochemical processes that are spatially and temporally variable influence the uptake of anthropogenic CO$_2$ from the atmosphere by the global ocean (e.g., Sabine and Tanhua, 2010; Tanhua et al., 2013) and exhibit feedbacks that can significantly impact Earth’s climate system in the future. The scale of sequestration of anthropogenic CO$_2$ by the ocean and terrestrial biosphere over the next few centuries is slowly being understood through the systematic collection of time-series observations that quantify the uncertainties in physico-biogeochemical feedbacks in the atmosphere-terrestrial biosphere-ocean system. These measurements are required to help predict scenarios about future CO$_2$ emissions, socio-economic drivers of CO$_2$ release, and evolving mitigation/adaptation strategies.

The uptake of anthropogenic CO$_2$ from the atmosphere by the global ocean also has significant implications for surface ocean chemistry, individual marine organisms, and ocean ecosystems. The ocean’s pH is controlled by the acid-base buffering capacity of seawater that in turn is primarily controlled by equilibrium reactions of CO$_2$ with seawater. These reactions give rise to a chemical system that involves carbonic acid [H$_2$CO$_3$], carbonate ion [CO$_3^{2-}$], and bicarbonate ion [HCO$_3^{-}$] (Box 1; Zeebe and Wolf-Gladrow, 2001). At present, the global ocean remains generally mildly alkaline, with a pH of surface waters typically in the range of 8.1 to 8.2. However, the uptake of anthropogenic CO$_2$ by seawater alters the natural chemical equilibrium of the present-day seawater CO$_2$-carbonate system, resulting in gradual acidification of seawater in a process termed “ocean acidification” (OA; e.g., Caldeira and Wickett, 2003; Doney et al., 2009).

Ocean acidification can be viewed as a decrease of the chemical bases in seawater that results in increasing protons (H$^+$) and reduction of pH. It also decreases the CO$_3^{2-}$ concentration and saturation state ($\Omega$) of calcium carbonate (CaCO$_3$) minerals such as calcite ($\Omega_{\text{calcite}}$) and aragonite ($\Omega_{\text{aragonite}}$). Such changes in seawater chemistry have complex direct and indirect impacts on marine organisms and ecosystems (e.g., Gattuso and Hansson, 2011).

Sustained time-series observations provide a wealth of data about ocean physics and biogeochemistry that can be used to examine, test, and refine many paradigms and hypotheses about the functioning of the ocean. Such time series generate information not only about ocean warming and water cycle reorganization (e.g., salinity changes), ocean eutrophication, and ocean deoxygenation but also about changes in surface ocean chemistry. In this article, we examine recent changes in surface seawater CO$_2$-carbonate chemistry at the locations of seven ocean CO$_2$ time series that have been gathering sustained observations from 15 to 30 years (Figure 1). This cohort of ocean time-series sites exhibits consistent changes in surface ocean chemistry that reflect the impact of uptake of anthropogenic CO$_2$ and ocean acidification.

The ocean CO$_2$ time series considered here are based on shipboard observations and include two sites in the subpolar North Atlantic Ocean (Figure 1; Iceland Sea and Irminger Sea; Olafsson et al., 2009, 2010) and five sites in tropical/sub-tropical/temperate waters of the North Atlantic and Pacific Oceans (Figure 1; (1) Bermuda Atlantic Time-series Study [BATS], Bates et al., 2012; (2) European Station for Time Series in the Ocean near the Canary Islands [ESTOC], González-Dávila et al., 2010; (3) Hawaii Ocean Time-series [HOT], Dore et al., 2009; (4) CArbon Retention In A Colored Ocean [CARIACO], Cariaco Basin, Astor et al., 2005, 2013; Muller-Karger et al., 2010; Taylor et al., 2012; and (5) Munida, R/V Munida time series, Currie et al., 2011). While we focus here on surface observations, the entire water column from surface to near the seafloor is typically sampled with a frequency that ranges from approximately four to 16 repeat occupations of each site per year (Table 1). Thus, individual time series are integrated studies with a broad suite of sustained water-column observations, including hydrography, biogeochemistry (e.g., dissolved oxygen, inorganic nutrients, chlorophyll, and dissolved and particulate organic carbon and nitrogen), and rate measurements (including $^{14}$C primary production, bacterial production, and organic matter export flux), and various taxonomic and molecular observations. Therefore, our cohort of ocean CO$_2$ time-series programs benefits from synergies and connectivity with broad understanding gained about ocean physics, biology, and chemistry at each site. As aptly noted by many earlier writers, “the sum is greater than the individual parts” when ocean time-series nodes are considered as a whole or as a nexus of scientific endeavor where substantial observations support concomitant process studies.
BOX 1. SEAWATER CO₂-CARBONATE CHEMISTRY

The chemical basis of the seawater CO₂-carbonate system is the reaction of CO₂ with water to form carbonic acid (H₂CO₃) and other carbonate species (Zeebe and Wolf-Gladrow, 2001). The chemical equilibria are defined as

\[
\text{CO}_2 \text{(gas)} \rightleftharpoons \text{CO}_2 \text{(aqueous)} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+ \quad (1)
\]

Dissolved inorganic carbon (DIC) is the sum of bicarbonate ([HCO₃⁻]), carbonate ([CO₃²⁻]), and CO₂ in natural waters (Dickson et al., 2007) and thus defined as

\[
\text{DIC} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] \quad (2)
\]

where [CO₃²⁻] is equivalent to [CO₂]aq + [H₂CO₃]. Total alkalinity (TA) can be defined in its simplest terms as

\[
\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}^-] + [\text{OH}^-] - [\text{H}^+] + \ldots \quad (3)
\]

where [B(OH)⁻] is total borate concentration in seawater and ‘…” reflects a suite of minor constituents that influence alkalinity (see Dickson et al., 2007, for a full definition of alkalinity).

DIC, TA, pH, and pCO₂ (partial pressure of CO₂) are the common measurable parameters, and all components of the seawater CO₂-carbonate system, including [HCO₃⁻], [CO₃²⁻], and saturation states for calcium carbonate (CaCO₃) minerals such as calcite (Ωcalcite) and aragonite (Ωaragonite), can be computed from any two of these measured parameters. Here, Ω is defined as

\[
[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_	ext{sp} \quad (4)
\]

where Ksp is the solubility product of calcite and aragonite, respectively. Physico-biogeochemical processes such as ocean release of CO₂ by air-sea gas exchange or fixation of CO₂ via photosynthesis (i.e., primary production) act to decrease DIC and pCO₂ and increase pH, Ωaragonite, and Ωcalcite (e.g., Zeebe and Wolf-Gladrow, 2001). In contrast, ocean uptake of CO₂ and respiration act oppositely (increasing DIC and pCO₂ and decreasing pH, Ωaragonite, and Ωcalcite), while TA remains unchanged (except for minor changes associated with nitrate uptake or release). Precipitation or calcification (i.e., the formation of CaCO₃ in shells, tests, or skeletons of organisms) and dissolution of CaCO₃ are defined by

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \quad (5)
\]

and

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3 \quad (6)
\]

with calcification/CaCO₃ precipitation reducing TA, and dissolution increasing TA.

Seawater CO₂-carbonate system parameters, including pCO₂ (μatm), Ωaragonite and Ωcalcite, and pH (total scale) were computed from salinity (S), temperature (T), TA, and DIC data using CO2calc software (Robbins et al., 2010). The carbonic acid dissociation constants pK₁ and pK₂ (Mehrbach et al., 1973, as refit by Dickson and Millero, 1987) were used for these computations. The DIC-TA pair was typically used to calculate pCO₂, pH, Ωaragonite, and Ωcalcite, but other observed pairs were also used for the computation (See Table 1). We estimated the calculation error range for pCO₂, pH, and Ωaragonite and Ωcalcite to be ±5 μatm ±0.001, and ±0.02 (assuming a DIC and TA analytical error of ±2 μmol kg⁻¹), respectively. pH is determined on the seawater pH, Ω aragonite, and Ω calcite (e.g., Zeebe and Wolf-Gladrow, 2001). In contrast, ocean uptake of Ω calcite, while TA remains unchanged (except for minor changes associated with nitrate uptake or release). Precipitation or calcification (i.e., the formation of CaCO₃ in shells, tests, or skeletons of organisms) and dissolution of CaCO₃ are defined by

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\[
\beta = \frac{\partial \delta \ln [\text{pCO}_2]}{\partial \delta \ln \text{DIC}} \quad (7)
\]

with higher Revelle factors indicating lower capacity of the ocean to absorb CO₂ (see Egleston et al., 2010, for further discussion on ocean CO₂ buffer capacity).

Ocean Data View 4 (ODV, http://odv.awi.de) software was used to visualize the data.

A BRIEF HISTORY OF SUSTAINED OCEAN CARBON CYCLE OBSERVATIONS

Sustained ocean time series began with repeated observations of select areas of the ocean and establishment of ocean weather station ship observations in the early half of the twentieth century. One of the first efforts was continuous plankton recorder (CPR) observation of ocean phytoplankton communities initiated by Sir Alistair Hardy in 1931—and continuing today (http://www.safhos.co.uk). The California Cooperative Oceanic Fisheries Investigations (CalCOFI; http://www.calcofi.org) organization was formed in 1949, and its hydrographic and biogeochemical sampling of the California coast commenced in earnest in the early 1960s; it also continues to present, as do other coastal programs, such as the Helgoland Roads time series in the North Sea (Wiltshire et al., 2010). In the open ocean, Henry Stommel of the Woods Hole Oceanographic Institution (WHOI) initiated water column sampling of hydrography (e.g., salinity, temperature) at Hydrostation S (known as the Panulirus site in its early days) off Bermuda in 1954 (e.g., Menzel and Ryther, 1964).

The first comprehensive survey and collection of seawater CO₂-carbonate chemistry in the open ocean occurred as part of the Geochemical Ocean Sections Study (GEOSECS; Takahashi et al., 1982), and it was followed soon thereafter by annual reoccupation of ocean sections such as Line P, initiated in 1973 in the North Pacific Ocean (Wong et al., 2010). The GEOSECS program provided the foundation for subsequent scientific expeditions such as the Transient Tracers in the Ocean (TTO) expedition of the North and tropical Atlantic Oceans in the early
1980s (Brewer et al., 1985), and the World Ocean Circulation Experiment (WOCE) and Joint Global Ocean Flux Study (JGOFS) in the late 1980s and 1990s. The initiation of time series such as BATS and HOT in the late 1980s and subsequent expansion of sustained observations around the globe owe much to these earlier efforts and to the growing recognition that understanding of the time-varying components of the ocean carbon cycle and related inorganic nutrient dynamics (e.g., nitrogen, phosphorus, and silica) required identification of the relevant physical, chemical, and ecosystem processes responsible for observed variability.

Several other factors promoted the expansion of ocean CO₂ time series (including repeating ocean sections) in both open-ocean and coastal environments in order to detect changes in the ocean carbon cycle due to both natural processes and anthropogenic perturbation. Improvements in chemical instrumentation (e.g., Johnson et al., 1987, 1993) allowed sample analyses to be conducted with sufficient sensitivity to detect gradual change. These developments were complemented by rigorous standard operating protocols for chemical analysis (Dickson et al., 2007) and refinement of chemical equilibria models of the seawater CO₂-carbonate system (e.g., Zeebe and Wolf-Gladrow, 2001). In the early 1990s, Andrew Dickson of Scripps Institution of Oceanography (SIO) developed and distributed certified reference material (CRMs)—seawater with carefully measured and standardized DIC and TA concentrations that allowed assessments to be made of the long-term accuracy of other measurements. Incorporation of seawater CO₂-carbonate chemistry data into global climatology products such as the Global Ocean Data Project (GLODAP; Key et al., 2004; Sabine et al., 2005) and PACIFICA (PACIfic ocean Interior Carbon; Suzuki et al., 2013) is credited as critically important for improvement of global models and for understanding global ocean carbon cycle feedbacks and synergies necessary to detect changes in the ocean carbon cycle due to both natural processes and anthropogenic perturbation (e.g., Sabine and Tanhua, 2010; Tanhua et al., 2013).

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SEASONAL AND LONG-TERM CHANGES IN SURFACE SEAWATER CO₂-CARBONATE CHEMISTRY

Types of Time-Series and Repeated Ocean Section CO₂ Observations

Sustained, high-accuracy observations of seawater CO₂-carbonate chemistry changes extend three decades into the past. Here, we focus on surface ocean CO₂ observations that have been carried out with relatively high frequency (monthly or seasonal sampling) in fixed ocean time series that include comprehensive ocean biogeochemistry and ecology data collection (Table 1; Iceland Sea, Irminger Sea, BATS, ESTOC, HOT, CARIACO, and Munida). Importantly, these ocean CO₂ time series contribute to understanding of the dynamics of the ocean carbon cycle and related nutrient cycles, and the continuing elucidation of the paradigms and model function of each ocean system. Several other relatively high-frequency ocean time-series sites not included in this review are DYFAMED (DYnamic des Flux Atmosphériques en MEDITerranée, Mediterranean Sea, Touratier and Goyet, 2009), KNOT (Kyodo North Pacific Time-series, Wakita et al., 2005; Watanabe et al., 2011), and other Pacific Ocean sites (e.g., Ishii et al., 2011; Midorikawa et al., 2012).

Other time-series data have also contributed to establishing long-term trends in seawater CO₂-carbonate chemistry (see online Supplementary Table S1 for details), including: (1) annual reoccupations of a fixed location or ocean section (e.g., Line P, North Pacific Ocean, Wong et al., 2010; Ocean Weather Station Mike, Norwegian Sea, Skjelvan et al., 2008), (2) long-term opportunistic surface sampling efforts that are irregular in time and space but sufficient to establish long-term trends in ocean regions (e.g., surface pCO₂ trends; Takahashi et al., 2009; McKinley et al., 2011), and (3) lower-frequency sampling along an ocean section reoccupied through projects like WOCE and CLIVAR/CO₂ Repeat Hydrography (e.g., North Pacific Ocean: Byrne et al., 2010; Midorikawa et al., 2012; Rockall Trough: McGrath et al., 2012; Southern Ocean: van Heuven et al., 2011). Ocean climate stations such as HOT (Hawaii, Pacific Ocean, 2003–present), KEO (Kuroshio Extension Observatory, North Pacific Ocean, 2004–present), and Ocean Station Papa (50°N, 145°W, 2007–present) represent emerging moored surface seawater CO₂-carbonate chemistry data collection systems that will provide multidecadal understanding in the future.

How to Establish Trends in Surface Seawater CO₂-Carbonate Chemistry Using Irregularly Sampled Seasonal Data

The seven comprehensive surface ocean biogeochemistry and ecology time series highlighted in this paper have a frequency of occupation ranging from three or four times per year to as many as 16 times per year, often with irregularly spaced sampling times. The irregularity of sampling, non-uniform time intervals between cruises, and considerable seasonality (e.g., at BATS, Bates et al., 1996; at HOT, Dore et al., 2003; at Munida, Brix et al., 2013; Figure 2) exhibited at each time-series site complicates statistical trend analyses of seawater CO₂-carbonate chemistry data. For example, at the BATS site, additional bloom cruises increase the sampling frequency to bimonthly during the January to April period, which

<table>
<thead>
<tr>
<th>Time-Series Site</th>
<th>Sampling Region</th>
<th>Location</th>
<th>Time Series Duration</th>
<th>Frequency (per year)</th>
<th>Principal Scientists</th>
<th>Ocean C Cycle Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iceland Sea</td>
<td>Iceland Sea</td>
<td>68°N, 12.66°W</td>
<td>1983–present</td>
<td>3–4</td>
<td>J. Olafsson</td>
<td>DIC/pCO₂</td>
</tr>
<tr>
<td>Irminger Sea</td>
<td>Irminger Sea</td>
<td>64.3°N, 28°W</td>
<td>1983–present</td>
<td>3–4</td>
<td>J. Olafsson</td>
<td>DIC/pCO₂</td>
</tr>
<tr>
<td>ESTOC</td>
<td>Canary Islands</td>
<td>29.04°N, 15.50°W</td>
<td>1995–present</td>
<td>4–6</td>
<td>M. González-Dávila, M. Santana-Casiano</td>
<td>DIC/TA</td>
</tr>
<tr>
<td>HOT</td>
<td>North Pacific</td>
<td>22°45'N, 158°W</td>
<td>1988–present</td>
<td>10</td>
<td>J. Dore, M. Church</td>
<td>TA/pH</td>
</tr>
<tr>
<td>CARIACO</td>
<td>Cariaco Basin</td>
<td>10°30'N, 64°40'W</td>
<td>1995–present</td>
<td>12</td>
<td>Y. Astor, L. Lorenzoni, F. Muller-Karger</td>
<td>TA/pH</td>
</tr>
<tr>
<td>Munida</td>
<td>South Pacific</td>
<td>45.7°S, 171.5°E</td>
<td>1998–present</td>
<td>~ 4–6</td>
<td>K. Currie, K. Hunter</td>
<td>pCO₂/TA</td>
</tr>
</tbody>
</table>

Relevant Web addresses for data access:
Irminger Sea: http://cdiac.ornl.gov/oceans/Moorings/Iceland_Sea.html
Iceland Sea: http://cdiac.ornl.gov/oceans/Moorings/Irminger_Sea.html
BATS: http://www.bios.edu/research/projects/bats
HOT: http://hahana.soest.hawaii.edu/hot/hot_jgosf.html
ESTOC: http://www.eurosites.info/estoc.php
CARIACO: http://www.imars.usf.edu/CAR/index.html
Munida: http://cdiac.ornl.gov/oceans/Moorings/Munida.html
Seasonality of Hydrography and Seawater CO₂-Carbonate Chemistry

The data from the ocean CO₂ time-series sites exhibit seawater CO₂-carbonate chemistry that reflects different environments ranging from subpolar water (Iceland Sea, Irminger Sea), to subtropical gyre (BATS, ESTOC, HOT), and a semi-enclosed marginal tropical sea (CARIACO in the Caribbean Sea; Figure 1). Figure 2 shows mean climatological hydrographic properties (salinity and temperature), seawater CO₂-carbonate chemistry parameters (DIC, nDIC, pCO₂, pH, and Ω<sub>aragonite</sub>), and the buffering capacity of the ocean (Revelle factor, β) for the period of observation at each individual time-series site. The
seasonality of hydrography and the seawater CO$_2$-carbonate system (as well as of inorganic nutrients, phytoplankton community structure, biomass, and rate of primary, new, and export production, for example) at each time-series site has been reported in many previous studies (e.g., Steinberg et al., 2001; Astor et al., 2005; Muller-Karger et al., 2010; Taylor et al., 2012; Church et al., 2013; Lorenzoni et al., 2013; see references within these papers). Here, we briefly compare the seasonality evident at the cohort of time-series sites as context for a later discussion of long-term trends in the ocean carbon cycle.

**Salinity and Temperature**

Five of the time series had low salinity seasonality (< 0.1), while the BATS and CARIACO sites had considerable seasonal variability. This variability was caused by winter mixing at BATS, upwelling at the CARIACO site, and fresher surface waters in summer/fall due to increased precipitation at both sites (Figure 2a). The latitudinal gradient between time series was pronounced for temperature, with all sites exhibiting seasonality (to ~8°C). The Iceland Sea (~6°C) and BATS (~8°C) had the highest seasonal temperature variability (Figure 2b).

**DIC and nDIC**

The range of DIC and nDIC varied from ~1,980 to ~2,150 μmol kg$^{-1}$ for the seven time-series sites (Figure 2c,d). With the exception of HOT, all other time series showed considerable seasonal variability for DIC and nDIC (Figure 2c,d), ranging from < 10 to ~60 μmol kg$^{-1}$ (with the subpolar time-series sites exhibiting the largest seasonality of hydrography and the seawater CO$_2$-carbonate system (as well as of inorganic nutrients, phytoplankton community structure, biomass, and rate of primary, new, and export production, for example) at each time-series site has been reported in many previous studies (e.g., Steinberg et al., 2001; Astor et al., 2005; Muller-Karger et al., 2010; Taylor et al., 2012; Church et al., 2013; Lorenzoni et al., 2013; see references within these papers). Here, we briefly compare the seasonality evident at the cohort of time-series sites as context for a later discussion of long-term trends in the ocean carbon cycle.

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**DIC and nDIC**

The range of DIC and nDIC varied from ~1,980 to ~2,150 μmol kg$^{-1}$ for the seven time-series sites (Figure 2c,d). With the exception of HOT, all other time series showed considerable seasonal variability for DIC and nDIC (Figure 2c,d), ranging from < 10 to ~60 μmol kg$^{-1}$ (with the subpolar time-series sites exhibiting the largest
winter in the subtropical gyre (e.g., Winn et al., 1994; Bates, 2007; Santana-Casiano et al., 2007; Dore et al., 2009). At BATS and ESTOC, summertime warming increases surface $pCO_2$, so these waters seasonally transition to being a weak source of CO$_2$ to the atmosphere for a few months each year. This also occurs at the HOT site during the warmest months when the surface ocean briefly transitions to being a weak source of CO$_2$ to the atmosphere. In contrast to the other subpolar sites, high Revelle factor values indicate relatively reduced efficiency of absorption of CO$_2$ from the atmosphere, but the large air-sea CO$_2$ gradients at the subpolar time series facilitate strong uptake of CO$_2$ from the atmosphere (Olafsson et al., 2010). In contrast, subtropical waters, with lower Revelle factor values, have the highest capacity to absorb CO$_2$ per unit volume of seawater.

The Revelle factor or buffering capacity of surface waters was highly variable, ranging from $\sim$ 9–10 in the subtropics to $\sim$ 12–15 at the subpolar time-series sites where there was pronounced seasonality (Figure 2f). Similar latitudinal gradients have been shown previously (e.g., Sabine et al., 2004), with the higher Revelle factor values reflecting reduced capacity to absorb CO$_2$ from the atmosphere. This seeming contradiction reflects the complexities of the CO$_2$-carbonate equilibria in seawater. At the subpolar sites, high Revelle factor values indicate relatively reduced efficiency of absorption of CO$_2$ from the atmosphere, but the large air-sea CO$_2$ gradients at the subpolar time series facilitate strong uptake of CO$_2$ from the atmosphere (Olafsson et al., 2010). In contrast, subtropical waters, with lower Revelle factor values, have the highest capacity to absorb CO$_2$ per unit volume of seawater.

$pH$ and $\Omega_{aragonite}$

Surface water pH was lowest at the CARIACO site ($\sim$ 8.02 to 8.05), while the highest seasonal values were observed at BATS and the two subpolar sites (up to 8.16; Figure 2g); pH seasonality was considerable at these latter sites. As expected from the equilibrium thermodynamics of the seawater CO$_2$-carbonate system, surface $pCO_2$ and pH exhibit mirrored seasonal changes (Figure 2e,g). For $\Omega_{aragonite}$, large differences are evident between the subpolar sites ($\sim$ 1.5 to 2.5) and the subtropical sites ($\sim$ 3.3 to $\sim$ 4.0), with most sites exhibiting considerable seasonality as demonstrated for other parameters such as DIC, nDIC, pCO$_2$, and pH. Note that the long-term changes in pH and $\Omega_{aragonite}$ due to ocean acidification, discussed later, have to be viewed in the context of large natural seasonal variability at most of the sites.

Table 2. (A) Seawater CO$_2$-carbonate seawater trends and standard error for the seven ocean time-series sites listed in Table 1. (B) Regression statistics $r^2$ ($r^2$ values of $>0.30$ are in bold type), n (number of samples), and $p$-value are given (* = $p$-value $<0.01$; § = $p$-value $>0.01$, not statistically significant). The seawater CO$_2$-carbonate seawater parameters were seasonally detrended to remove seasonality of the observations and calculated parameters. In the method, climatological mean values were determined for data collected at individual time-series sites during each of four seasons (January to March, April to June, July to September, October to December). The observed values were then compared to mean values to determine anomalies in the seawater CO$_2$-carbonate seawater parameters. Similar methods have been used previously to determine trends from seasonally impacted and irregularly sampled data in time (e.g., Bates et al., 2012). nDIC is salinity normalized DIC corrected to the mean salinity observed at each individual time-series site.

<table>
<thead>
<tr>
<th>Time-Series Site</th>
<th>DIC (µmol kg$^{-1}$ yr$^{-1}$)</th>
<th>nDIC (µmol kg$^{-1}$ yr$^{-1}$)</th>
<th>$pCO_2$ (µatm yr$^{-1}$)</th>
<th>Revelle Factor</th>
<th>pH</th>
<th>$\Omega_{aragonite}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Time-Series Ocean Carbon Cycle Trends</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iceland Sea</td>
<td>1.22 ± 0.27</td>
<td>0.93 ± 0.24</td>
<td>1.29 ± 0.36</td>
<td>0.019 ± 0.001</td>
<td>−0.0014 ± 0.0005</td>
<td>−0.0018 ± 0.0027</td>
</tr>
<tr>
<td>Irminger Sea</td>
<td>1.62 ± 0.35</td>
<td>1.49 ± 0.35</td>
<td>2.37 ± 0.49</td>
<td>0.030 ± 0.012</td>
<td>−0.0026 ± 0.0006</td>
<td>−0.0008 ± 0.0040</td>
</tr>
<tr>
<td>BATS</td>
<td>1.37 ± 0.07</td>
<td>1.12 ± 0.04</td>
<td>1.69 ± 0.11</td>
<td>0.014 ± 0.001</td>
<td>−0.0017 ± 0.0001</td>
<td>−0.0095 ± 0.0007</td>
</tr>
<tr>
<td>ESTOC</td>
<td>1.09 ± 0.10</td>
<td>1.08 ± 0.08</td>
<td>1.92 ± 0.24</td>
<td>0.019 ± 0.002</td>
<td>−0.0018 ± 0.0002</td>
<td>−0.0115 ± 0.0023</td>
</tr>
<tr>
<td>HOT</td>
<td>1.78 ± 0.12</td>
<td>1.05 ± 0.05</td>
<td>1.72 ± 0.09</td>
<td>0.014 ± 0.001</td>
<td>−0.0016 ± 0.0001</td>
<td>−0.0084 ± 0.0011</td>
</tr>
<tr>
<td>CARIACO</td>
<td>0.64 ± 0.40</td>
<td>1.89 ± 0.45</td>
<td>2.95 ± 0.43</td>
<td>0.011 ± 0.003</td>
<td>−0.0025 ± 0.0004</td>
<td>−0.0066 ± 0.0028</td>
</tr>
<tr>
<td>Munida</td>
<td>0.88 ± 0.30</td>
<td>0.78 ± 0.30</td>
<td>1.28 ± 0.33</td>
<td>0.028 ± 0.008</td>
<td>−0.0013 ± 0.0003</td>
<td>−0.0085 ± 0.0026</td>
</tr>
<tr>
<td>B. Statistics for Above Trends ($r^2$, n, and * = statistically significant $p$-value $&lt;0.01$ level)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iceland Sea</td>
<td>0.18 (91)*</td>
<td>0.23 (91)*</td>
<td>0.14 (84)*</td>
<td>0.06 (83)*</td>
<td>0.09 (83)*</td>
<td>0.05 (83)*</td>
</tr>
<tr>
<td>Irminger Sea</td>
<td>0.18 (101)*</td>
<td>0.15 (101)*</td>
<td>0.21 (87)*</td>
<td>0.07 (83)*</td>
<td>0.18 (82)*</td>
<td>0.05 (83)*</td>
</tr>
<tr>
<td>BATS</td>
<td>0.55 (373)*</td>
<td>0.64 (373)*</td>
<td>0.39 (378)*</td>
<td>0.44 (378)*</td>
<td>0.35 (378)*</td>
<td>0.35 (378)*</td>
</tr>
<tr>
<td>ESTOC</td>
<td>0.46 (152)*</td>
<td>0.55 (152)*</td>
<td>0.30 (152)*</td>
<td>0.51 (152)*</td>
<td>0.30 (152)*</td>
<td>0.43 (152)*</td>
</tr>
<tr>
<td>HOT</td>
<td>0.49 (232)*</td>
<td>0.62 (232)*</td>
<td>0.62 (232)*</td>
<td>0.51 (232)*</td>
<td>0.55 (232)*</td>
<td>0.39 (232)*</td>
</tr>
<tr>
<td>CARIACO</td>
<td>&lt; 0.05 (159)*</td>
<td>0.10 (153)*</td>
<td>0.24 (153)*</td>
<td>0.06 (153)*</td>
<td>0.20 (153)*</td>
<td>0.04 (153)*</td>
</tr>
<tr>
<td>Munida</td>
<td>0.10 (79)*</td>
<td>0.08 (79)*</td>
<td>0.17 (79)*</td>
<td>0.13 (79)*</td>
<td>0.16 (78)*</td>
<td>0.12 (79)*</td>
</tr>
</tbody>
</table>
MULTIDECADAL CHANGES IN SURFACE SEAWATER CO₂-CARBONATE CHEMISTRY

The longest of the ocean CO₂ time-series sites considered here extend back in time about 30 years. This time period is sufficient to establish seasonal and some interannual changes in seawater CO₂-carbonate chemistry that reflect changes in the natural carbon cycle and anthropogenic perturbation. Over relatively short time scales (< 10 years or so), observed trends in seawater CO₂-carbonate chemistry can be caused by natural variations of the carbon cycle imparted by climate modes of variability, and by variability of deep, intermediate, and mode water formation (e.g., Gruber et al., 2002; Bates et al., 2002; Bates, 2012). The impact of such phenomena on the ocean carbon cycle has been reported in many previous studies and includes the influence of, for example, the El Niño-Southern Oscillation (ENSO; e.g., Feely et al. 1994), the North Atlantic Oscillation (NAO; e.g., Bates, 2001; Santana-Casiano et al., 2007; Levine et al., 2011), and the Pacific Decadal Oscillation (PDO; e.g., McKinley et al., 2006). Winn et al. (1994) first observed the variability of the ocean carbon cycle at HOT in response to subtropical gyre variability, and it can be seen in the quasi-decadal variation of surface DIC around the long-term trend (Dore et al., 2003, 2009).

Over multidecadal time scales, direct observations over the past 25 to 30 years indicate that surface seawater pCO₂ (and DIC) is increasing at a similar rate to the increase in atmospheric pCO₂ (Takahashi et al., 2009; McKinley et al., 2011; Bates et al., 2012). However, we are mindful that it is difficult to assess any longer time scale impact on ocean carbon cycle variability by such phenomena as the Atlantic Multidecadal Variability (AMV; McKinley et al., 2004, 2011;) and the Atlantic Meridional Overturning Circulation. At some of the time-series sites, the statistical significance of trends is weak, but when considered with statistically significant trends evident at other time-series sites (Table 2), the cohort of time series discussed here show very similar trends. As Table 2B shows, while only BATS, ESTOC, and HOT had r² values > 0.30 for trends, nearly all long-term trends were statistically significant with p-values < 0.01. We also compare these trends to trends derived from data collected from annual and episodic reoccupation of ocean sites or sections (Supplementary Table S1).

A further caveat is that trends estimated from two or more repeat occupations are likely to be subject to ocean variability and uncertainty imparted by seasonal and interannual variability, depending on the timing of sampling and the length of time between repeat occupation of ocean sections or specific ocean sites. Combined, the long-term changes in ocean CO₂ content (i.e., DIC, nDIC, pCO₂, and pH, or buffer capacity indicators such as Revelle factor values) exhibit globally consistent and coherent changes in response to the uptake of anthropogenic CO₂ by the ocean.

Figure 4. Trends of surface seawater CO₂-carbonate chemistry for seven ocean time series plotted against length of time series (years), including: Iceland Sea (purple), Iminger Sea (blue), BATS (cyan), ESTOC (green), HOT (orange), CARIACO (red) and Munida (pink). The standard errors of the trends are also shown in the figure with the regression statistics given in Table 2. (A) nDIC (μmoles kg⁻¹ yr⁻¹) trends indicated by square symbols. Seasonally detrended nDIC trends are also indicated for each time-series site with circle symbols. (B) pCO₂ (µatm yr⁻¹) trends indicated by square symbols. Revelle factor (yr⁻¹) trends are also shown for each time-series site with circle symbols. (C) pH (yr⁻¹) trends indicated by square symbols. (D) Ω_{aragonite} (yr⁻¹) trends indicated by square symbols (i.e., saturation state of CaCO₃ mineral).

Long-Term Trends in Surface DIC and nDIC at the Seven Time-Series Sites

At the Atlantic and Pacific Ocean time-series sites, surface/mixed-layer DIC has increased by +0.64 to +1.78 μmol kg⁻¹ yr⁻¹ (Table 2; Figures 3 and 4a), with some of this variability in trends reflecting salinity changes at...
The nDIC trends had a slightly higher range at +0.78 to +1.89 μmol kg\(^{-1}\) yr\(^{-1}\) (Table 2; Figures 3 and 4a). The largest increase in nDIC was observed at CARIACO, reflecting changes in the ventilation of Subtropical Underwater in the region (Astor et al., 2013). The second largest increase in nDIC was observed in the Irminger Sea and has been attributed to strengthening of winter mixing (Olafsson et al., 2010). The other time-series sites clustered at an increase of +0.78 to +1.12 μmol kg\(^{-1}\) yr\(^{-1}\) (HOT salinity increased by 0.005 yr\(^{-1}\); \(r^2 = 0.18\); all other salinity trend \(r^2\) values < 0.10). In summary, all seven time-series data exhibit positive trends in nDIC of ~0.78 to 1.89 μmol kg\(^{-1}\) yr\(^{-1}\) (e.g., Bates et al., 2012). The increase in DIC of ~0.78 to 1.89 μmol kg\(^{-1}\) yr\(^{-1}\) observed at the time-series sites represents a 1.5% to 2.5% increase over the last three decades, with larger impacts for surface \(\rho\)CO\(_2\) and \(pH\) as discussed later.

Long-term trends for DIC observed at sites of annual reoccupation (e.g., Line P) or episodic reoccupation sites yielded similar results to those observed in the ocean CO\(_2\) time-series sites. The range of DIC increase reported for 10 sites in the North Atlantic and Pacific Oceans was ~ +0.86 to +2.3 μmol kg\(^{-1}\) yr\(^{-1}\) (see Supplementary Table S1) over a variety of time scales of observation (~6 to ~20 years). As discussed by Tanhua et al. (2013), the shorter duration time-series data tend to chart highly variable trends, reflecting the difficulties of assessing long-term trends in regions where there is considerable short-term spatio-temporal variability and insufficient reoccupation of sites to evaluate change over time. Furthermore, the underlying interannual variability associated with climatic variations such as the NAO, ENSO, and PDO requires that observations be made over a sufficient duration to account for their influences.

Assessment of trends from annual reoccupation of ocean sites can also be complicated if the time of sampling is not the same each year, especially in ocean regions where there is large seasonal variability (refer to earlier section on How to Establish Trends in Seawater CO\(_2\)-Carbonate Chemistry Using Irregularly Sampled Seasonal Data). Sampling along sections such as Line P are not uniform in time each year (see Supplementary Table S1), and thus long-term trends are highly influenced by larger seasonal variability (for DIC and other seawater CO\(_2\)-carbonate parameters) than the secular changes due to uptake of anthropogenic CO\(_2\) or natural ocean basin variability over time scales of a few decades. The trends in DIC increase (as well as other seawater CO\(_2\)-carbonate chemistry parameters) tend to increase along Line P as well as in the records of other annual or episodic reoccupations that have low statistical significance. Nonetheless, they have important and meaningful value when viewed in the context of similar changes observed in the cohort of ocean CO\(_2\) time series. As discussed earlier regarding seasonality at individual time-series sites, collection of seasonal data provides a critically needed context for assessing robust trends over relatively short time scales of one to three decades.

**Figure 5.** Time series of surface seawater anomalies of \(\rho\)CO\(_2\) (colored symbols) and observed \(\rho\)CO\(_2\) (gray symbols; μatm), with trends (μatm yr\(^{-1}\)) reported in Table 2 shown in bottom left-hand corner of each panel. Seawater CO\(_2\)-carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site. Note that the scale of the CARIACO data anomalies is different from that of the other time-series.
30 years, surface seawater pCO₂ has increased by ~15–20%. At the ESTOC, HOT, and BATS sites, the increase in surface pCO₂ was similar to the increase observed in atmospheric pCO₂ (e.g., Dore et al., 2009; González-Dávila et al., 2010; Bates et al., 2012). These rates are also similar to those determined from the past three decades of seawater pCO₂ collected from shipboard underway seawater systems (e.g., Takahashi et al., 2009; McKinley et al., 2011). At some time-series sites, surface seawater pCO₂ (and DIC) has kept pace with the contemporaneous increase in atmospheric pCO₂ during the last two to three decades. The implication of this finding is that one of the two primary driving forces for air-sea CO₂ gas exchange (ΔpCO₂; the difference in pCO₂ between ocean and atmosphere) has remained fairly constant across the subtropical gyres.

In the Iceland Sea, surface seawater pCO₂ has not kept pace with atmospheric pCO₂ over time, favoring increased uptake of CO₂ from the atmosphere. Similarly, at the Munida site in the sub-Antarctic surface waters of the South Pacific Ocean off New Zealand, surface pCO₂ has increased at a rate lower than that of the atmosphere (partly due to a cooling trend of ~0.3°C per decade).

In contrast, surface seawater pCO₂ has increased at rates greater than the atmosphere in the Irminger Sea and in the Cariaco Basin. At the CARIACO site, earlier estimates of the trend in pCO₂ have lower values (+1.77 ±0.43; 1996–2008; Astor et al., 2013) than those estimated for the period 1996–2012 (Table 2). As Figure 2 shows, these trends suggest that the potential for ocean uptake of CO₂ has decreased in the Irminger Sea over time, while the potential for efflux of CO₂ to the atmosphere in the Caribbean Sea at CARIACO may have increased slightly in the last few years.

The global complexity and heterogeneity of changes in surface pCO₂ and sinks and sources of atmospheric/anthropogenic CO₂ is further evidenced by the variability exhibited at annual reoccupation or episodic reoccupation sites (Supplementary Table S1). The rates of change vary from ~0.5 to 2.6 μatm yr⁻¹. The ΔpCO₂ gradients across the global ocean are highly variable over the short term, and the sink for CO₂ over the last couple of decades has been decelerating or accelerating for select periods (Olsen et al., 2003; Schuster and Watson, 2007; Watson et al., 2009; Schuster et al., 2013). In the Pacific Ocean, short-term variability in ΔpCO₂ gradients and sinks and sources of CO₂ appear strongly influenced by physical changes in the ocean basin (salinity changes associated with changes in evaporation versus precipitation at HOT; Dore et al., 2003; Midorikawa et al., 2005, 2012; Currie et al., 2011) and associated with ENSO and PDO changes (Feely et al., 1999, 2006; McKinley et al., 2006; Takahashi et al., 2009).

The seven ocean CO₂ time series analyzed here show different trends in surface pCO₂, but, universally, they also show positive increases in the Revelle factor (Figures 4b and 6), ranging from +0.011 yr⁻¹ to +0.019 yr⁻¹. The exception is the Irminger Sea, which exhibits greater increases in the Revelle factor of 0.030 yr⁻¹, reflecting the highest rate of surface pCO₂ increases (Figure 4b). The increase in Revelle factor indicates that the buffering capacity of subtropical to subpolar surface waters to absorb CO₂ has gradually reduced over time. This confirms theoretical considerations of the global ocean response to continued uptake of anthropogenic CO₂ from the atmosphere. It also confirms previous
model studies that predict an increasing trend in Revelle factor and reduction of the ocean’s capacity to absorb CO₂ at the BATS site and for the North Atlantic Ocean over time (Thomas et al., 2007).

Long-Term Trends in Surface pH and Ω_{aragonite} (A Response to Gradual Ocean Acidification)

The slow acidification of the surface ocean is evident at the seven ocean CO₂ time-series sites (Figures 4c and 7; Table 2). As anticipated from model predictions on changing seawater pH due to uptake of anthropogenic CO₂ (Caldeira and Wickett, 2003), surface seawater pH has declined at rates of –0.0013 yr⁻¹ to –0.0025 yr⁻¹. Over the last three decades, such pH changes in the surface ocean indicate that the hydrogen ion concentration of the ocean has increased by ~ 20% to 35%, depending on the ocean region. As shown for surface pCO₂ time series with the highest rates of increase in pCO₂ (Irminger Sea, CARIACO) have the highest rate of pH decrease (up to –0.0025 yr⁻¹ or about –0.025 pH decade⁻¹).

At CARIACO, lower pH is expected because of the upwelling of Subtropical Underwater, which is rich in DIC, and yet pH has continued to decrease in this region despite reduced upwelling and primary productivity decrease over the last decade (Taylor et al., 2012). The Iceland Sea, BATS, HOT, ESTOC, and Munida sites have a rather narrow range of pH decline, with rates of –0.0013 to –0.0018 yr⁻¹. Contemporaneous with such changes in ocean pH are similar declines in carbonate ion concentration ([CO₃²⁻], not shown here) and saturation state for calcium carbonate (CaCO₃) minerals such as aragonite (Ω_{aragonite}; Figures 4d and 8). Ω_{aragonite} values have declined at all time-series sites within a range of –0.0066 to –0.0115 yr⁻¹. The changes in pH and Ω_{aragonite} have long-term and gradual direct (and indirect) impacts on marine organisms and ecosystems, especially calcifiers and environments dominated by calcification or dissolution of CaCO₃ (e.g., Andersson et al., 2008; Gattuso and Hansson, 2011). The long-term changes in pH and Ω_{aragonite} superimpose their impacts (either mitigating or enhancing pH and Ω_{aragonite} decreases) on seasonal changes observed in the open ocean (e.g., Feely et al., 1988), upwelling systems (e.g., Feely et al., 2008), or coastal environments strongly impacted by high rates of primary production and export of organic carbon (e.g., Bates et al., 2009, 2013).

CONCLUSIONS AND OUTLOOK

Ocean CO₂ time-series data are important for understanding the rate of uptake of CO₂ and for ground truthing indirect assessments of the rate of the ocean’s uptake and inventories of anthropogenic CO₂ (Tanhua et al., 2013). On societally relevant time scales (i.e., decades to centuries), physical, chemical, and biological processes sequester large quantities of atmospheric CO₂ (including anthropogenic CO₂) into the ocean. Several indirect methods exist to determine the rates of uptake and cumulative inventories of anthropogenic CO₂ in the global ocean, including back calculation (e.g., ΔC*, MIX, TrOCA) and tracer-based (e.g., transit-time distributions [TTDs] estimates; Sabine and Tanhua, 2010). Estimates of the uptake of anthropogenic CO₂ vary from 0.1 to 2.3 mol C m⁻² yr⁻¹ (Tanhua et al., 2013; references therein), reflecting not only the spatio-temporal variability of sinks and sources in the global ocean (e.g., Takahashi et al., 2009) but also significant uncertainties and caveats in rate and inventory estimates.
The cohort of seven comprehensive ocean biogeochemistry- and ecology-based CO₂ time-series sites considered here have exhibited similar changes in surface seawater chemistry over the last three decades. Although based in different geographical locations and oceanic biomes, these time series provide some of the best information we have about temporal variability of ocean CO₂, and thus provide unprecedented understanding of the response of the ocean carbon cycle to natural variability and anthropogenic perturbation. The DIC and pCO₂ content of surface waters has increased in most sites at a similar rate in response to changes in atmospheric pCO₂ induced by the release of anthropogenic CO₂. The exceptions are the Irminger Sea and the CARIACO sites, where DIC and pCO₂ have increased at a rate higher than expected from equilibration with increasing atmospheric pCO₂ contents. This is due to the compounding effects of changes in the biological and physical factors at play at these locations (Astor et al., 2013). At the same time, the ocean’s capacity to absorb CO₂ from the atmosphere has declined, as evidenced by the ubiquitous increases in Revelle factor values. These observations confirm model predictions for changing surface ocean chemistry and the declining future ability of the global ocean to absorb the anthropogenic CO₂ transient in the atmosphere. The cohort of seven ocean CO₂ time series also exhibit significant long-term decreases in pH and saturation states for CaCO₃ minerals in response to ocean acidification and uptake of anthropogenic CO₂.

Looking into the future, climate variability and accompanying changes in ocean chemistry define a requirement for sustained, seasonally robust, long-term observations to determine rates of uptake of anthropogenic CO₂, ocean storage of anthropogenic CO₂, and the chemical context for the complex impacts on and responses of marine organisms and ecosystems to ocean acidification. Emerging technologies and autonomous sensors will complement shipboard sampling of the seawater CO₂-carbonate system in the next decade or two, providing seasonal and greater spatial context for understanding changes in the ocean carbon cycle. In time, these evolving technologies will likely provide sensors that can observe pH and pCO₂ with sufficient sensitivity and accuracy to contribute to the assessment of long-term global ocean changes in seawater chemistry. New satellite-based sensors are urgently needed to accomplish repeated, frequent, long-term observations over synoptic scales. Ocean climate stations such as those at the Papa and KEO sites in the North Pacific Ocean, and data assimilation studies of existing and future surface pCO₂ data such as those entrained into the Surface Ocean Carbon Atlas (SOCAT; e.g., Bakker et al., 2013), will improve understanding of the spatio-temporal variability of pCO₂ (i.e., Rödenbeck et al., 2013) and of interannual changes. These data products combined with ocean time series and autonomous sensor data will provide a powerful cohort of observations that will allow detailed assessments of changing surface ocean chemistry to be made in the open ocean and coastal seas in the future.

Figure 8. Time series of surface seawater anomalies of Ωaragonite (saturation state of CaCO₃ mineral; colored symbols) and observed Ωaragonite (gray symbols; no units), with trends (yr⁻¹) reported in Table 2 shown in top right-hand corner of each panel. Seawater CO₂-carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site.
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NRB is indebted to the many colleagues who have contributed to the BATS and Hydrostation S programs. Dave Keeling was instrumental in starting ocean CO2 measurements at Hydrostation S in 1983, and our use of a combined Hydrostation S/BATS time series owes a great debt to his foresight. Peter Brewer and Catherine Goyet are thanked for their early measurements of DIC and alkalinity at BATS. The past and present principal investigators of the BATS and Hydrostation S programs are thanked for their diligence in maintaining ocean time-series off Bermuda and includes Tony Knap, Tony Michaels, Dennis Hansell, Craig Carlson, Debbie Steinberg, Michael Lomas, and especially Rod Johnson, who has been critical to the success of BATS and Hydrostation S over the past 25 years. ESTOC started as a collaborative program among four European Institutions, the IFM-­Kiel, the University of Bremen, the Instituto Español de Oceanografía, and the Instituto Canario de Ciencias Marinas. MGD and JMSC were invited to contribute to ESTOC in October 1995 and are deeply grateful to O. Llinás from ICCM for that opportunity and to many other colleagues who have helped them. Several people have been instrumental to the quality and longevity of the HOT program CO2 measurements, including David Karl, Roger Lukas, Chris Winn, Dale Hebel, and Dan Sadler. JÓ is grateful for the cooperation of many colleagues at the Marine Research Institute in Iceland in the time-series work through all seasons since 1983. FM-K and YA are equally indebted to the many sailors and administrators who have contributed to sustaining the CARIACO program. The Munida time series is a joint program between NIWA and the University of Otago. Keith Hunter and Malcolm Reid have been involved with this time series since its inception. The program managers who had the vision to initiate support for the time series stations have had profound influence on ocean time series.

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REFERENCES


