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Changes in Ocean Heat, Carbon Content, and Ventilation: A Review of the First Decade of GO-SHIP Global Repeat Hydrography*

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Keywords

anthropogenic climate change, ocean temperature change, salinity change, ocean carbon cycle, ocean oxygen and nutrients, ocean chlorofluorocarbons, ocean circulation change, ocean mixing

Abstract

Global ship-based programs, with highly accurate, full water column physical and biogeochemical observations repeated decadally since the 1970s, provide a crucial resource for documenting ocean change. The ocean, a central component of Earth's climate system, is taking up most of Earth's excess anthropogenic heat, with about 19% of this excess in the abyssal ocean beneath 2,000 m, dominated by Southern Ocean warming. The ocean also has taken up about 27% of anthropogenic carbon, resulting in acidification of the upper ocean. Increased stratification has resulted in a decline in oxygen and increase in nutrients in the Northern Hemisphere thermocline and an expansion of tropical oxygen minimum zones. Southern Hemisphere thermocline oxygen increased in the 2000s owing to stronger wind forcing and ventilation. The most recent decade of global hydrography has mapped dissolved organic carbon, a large, bioactive reservoir, for the first time and quantified its contribution to export production (\sim 20%) and deep-ocean oxygen utilization. Ship-based measurements also show that vertical diffusivity increases from a minimum in the thermocline to a maximum within the bottom 1,500 m, shifting our physical paradigm of the ocean's overturning circulation.

1. INTRODUCTION

The ocean is variable on all temporal and spatial scales. This variability has both natural and anthropogenic causes. For climate variability and climate change, the global ocean, through its full depth, is singularly important for its role in heat storage and mediation of increasing anthropogenic CO_2 (C_{ant}) in the atmosphere. Single-point time-series stations have increased understanding of the patterns of temporal variability, but by their nature remain limited in the spatial domain. Satellite observations provide global coverage at relatively high temporal resolution, but are restricted to a few surface parameters. Autonomous floats have begun to provide nearly global coverage of temperature and salinity at ten-day intervals, but are currently limited to the upper 2,000 m (Roemmich et al. 2015). A ship-based observing system is the only technique at present for obtaining the necessary highly accurate measurements of physical and biogeochemical properties of the ocean, including carbon.

The Global Ocean Ship-Based Hydrographic Investigations Program (GO-SHIP; http:// www.go-ship.org) executes systematic decadal reoccupations of select hydrographic sections (see map in Supplemental Figure 1, included in Supplemental Appendix 1; follow the Supplemental Materials link from the Annual Reviews home page at http://www.annualreviews.org) with the goal of obtaining full-depth water column measurements of physical and chemical variables (see Supplemental Appendix 1). This program is a component of the Global Climate Observing System (GCOS) and Global Ocean Observing System (GOOS).

Beginning with a comparison of two pairs of zonal hydrographic sections taken some 25 years apart in the North Atlantic (Roemmich & Wunsch 1984), there has been ongoing documentation of the changing properties of the ocean, from the surface to the bottom. In combination with efforts from previous decades, the data emerging from the decadal GO-SHIP program have led to major scientific discoveries that have advanced our understanding of the roles of the ocean in climate change, carbon cycling, and biogeochemical responses to climate change. The GO-SHIP results outlined herein have been key in studies of (a) heat and freshwater storage and flux (Section 2), (b) circulation changes and mixing (Section 3), (c) sequestration of anthropogenic carbon and biogeochemical changes (Section 4), (d) ventilation of deep and shallow water masses (Section 5), and (e) oxygen and nutrient changes (Section 6), and have provided accurate data for (f) calibration and validation of models and (g) calibration and checks of autonomous sensors.

2. HEAT AND SALINITY

The ocean plays a primary role in taking up and storing heat on our planet. Temporal and spatial variability in ocean heat storage is linked to decadally varying atmospheric forcing and to the spatial pattern and variability of the ocean's overturning circulation (see Section 3). As a result of increases in anthropogenic greenhouse gases, Earth's energy budget is currently not in balance, with more energy being absorbed than returned to space.

Quantifying the planetary energy imbalance is an important part of the projections of how much and how fast the atmosphere will warm (e.g., Frölicher et al. 2014) and anchors satellite measurements of the top-of-the-atmosphere energy imbalance (Loeb et al. 2012). Rhein et al. (2013) estimated that ocean warming took up 93% of that energy imbalance from 1971 to 2010, with 3% each going into melting ice and warming the continents and only 1% going into warming the atmosphere. The significance of the amount of heat stored in the deep ocean has become increasingly evident in the past several years (Purkey & Johnson 2010, Mauritzen et al. 2012). Although the upper ocean has taken up most of the excess heat, approximately 19% has gone into the deep ocean (>2,000 m).

Changes in Earth's heat balance are accompanied by changes in its water cycle. The ocean constitutes 70% of the planet's surface; most evaporation and precipitation occurs over the oceans. Seawater is a combination of freshwater and dissolved salts. The salts arise principally from weathering, and the total amount in the ocean has been effectively constant over millions of years. Therefore, ocean salinity, which is proportional to mass of salt per mass of seawater, is principally a measure of dilution of the salts by freshwater.

The ocean salinity distribution is set by the transport of freshwater through the atmosphere and ocean (e.g., Talley 2008). Variation in the hydrological cycle (evaporation, rainfall, and river discharge) and in the cryosphere (e.g., sea ice, glaciers, and ice sheets) is the principal cause for large-scale salinity change. The ocean is effectively a global rain gauge because it covers so much of Earth. A global assessment of changes in freshwater storage using several decades of hydrographic data has shown coherent large-scale patterns (Boyer et al. 2005, Bindoff et al. 2007). This signal has been more clearly delineated by adding data from the upper-ocean Argo profiling float network of the 2000s (Durack & Wijffels 2010). These changes are consistent with increased loss of freshwater from regions of net evaporation (midlatitudes) and its deposition in regions of net precipitation (higher latitudes). Furthermore, a zonal redistribution of freshwater from the saline Atlantic and Indian Oceans to the fresher Pacific has been documented (Bindoff et al. 2007, Durack et al. 2012). These are patterns expected in a warming climate (Rhein et al. 2013).

In the following sections, we focus on temperature and salinity changes in the deep ocean (>2,000 m) because these have been observable only through the use of multidecadal repeat hydrography data. Changes in temperature and salinity in the abyssal ocean are a significant fraction of the overall changes and result from changes in ventilation rates and properties of the waters that fill much of the deep global ocean (e.g., Johnson 2008). Temperature and salinity changes contribute to global and regional sea level rise through thermal expansion and haline contraction, and again, the contribution of the abyssal ocean is not negligible (Kouketsu et al. 2011, Purkey & Johnson 2013).

2.1. Deep-Ocean Warming

GO-SHIP has revealed prominent warming in abyssal waters around the globe (Figure 1*a*). The strongest warming is observed in the Southern Ocean near the source of Antarctic Bottom Water (Purkey & Johnson 2010). When integrated globally, the abyssal temperature increase of approximately $0.03 \,^{\circ}$ C decade⁻¹ in the deep basins around Antarctica amounts to an ~35-TW rate of warming below 2,000 m between the 1990s and 2000s. This is ~19% of the rate of warming of the entire climate system, which has been estimated as ~183 TW between 1972 and 2008 (Church et al. 2011).

Regionally, warming has been strongest in the deep western boundary currents (Kouketsu et al. 2011, Sloyan et al. 2013) and more generally in the western regions of the basins. In the North Atlantic this pattern may be reversed, with warming on the western side of the Mid-Atlantic Ridge



(*a*) Mean warming rates (°C per decade) below 4,000 m (*color bar*) estimated for deep ocean basins (*thin gray outlines*), centered on 1992–2005. Stippled basin warming rates are not significantly different from zero at 95% confidence. The positions of the repeat oceanographic transects from which these warming rates are estimated (*thick black lines*) are also shown. (Data from Purkey & Johnson 2010.) (*b*) Rates of freshwater inventory change (*colors*) resulting from water-mass (θ -S) changes within the Antarctic Bottom Water ($\theta < 0^{\circ}$ C) in deep basins (*outlined areas*), again estimated from repeat hydrographic sections, where θ is potential temperature and S is salinity. Panel *a* adapted from Rhein et al. (2013), based on Purkey & Johnson (2010); panel *b* adapted from Purkey & Johnson (2013).

(Johnson et al. 2008). Both patterns may imply a slowdown in the northward flow of abyssal water from Antarctica, as discussed in Section 3.1. A third set of occupations of these sections, starting in 2012, has allowed quantification of deep-ocean changes over longer time periods, such as the abyssal warming in the Brazil Basin observed from 1989 to 2014 (Johnson et al. 2014).

2.2. Deep-Ocean Salinity and Freshwater Changes

GO-SHIP repeat hydrography has enabled the full geographic and depth dependence of salinity changes to be observed. Salinity has increased in the subtropical salinity maxima of the South Indian and South Atlantic Oceans. Near-surface freshening has occurred in the Pacific subtropical salinity maxima (Nakano et al. 2015) and throughout the tropical Atlantic surface waters. The Southern Hemisphere pycnocline, at levels shallower than the Antarctic Intermediate Water, has freshened (Talley 2009, Helm et al. 2010). Oxygen and chlorofluorocarbon (CFC) changes at the same locations (see Sections 5 and 6.1) indicate that this thermocline freshening is likely related to increased ventilation from the south.

Deep salinity changes reflect changes in deep- and bottom-water formation rates and properties, and, like temperature, they can affect sea level through changes in density. In the Southern Hemisphere, freshening of bottom waters throughout the Ross Sea and Adélie Land sectors has been observed from the 1990s through the 2000s, whereas the Weddell Sea salinity has changed very little (**Figure 1***b*). The overall abyssal freshening for the Antarctic Bottom Water of potential temperature $\theta < 0^{\circ}$ C is equivalent to the addition of approximately 100 Gt year⁻¹ of freshwater [a rate of ~0.003 sverdrups (Sv); 1 Gt = 10^{12} kg, and 1 Sv ~ 10^{9} kg s⁻¹] (Purkey & Johnson 2013). This amount is a significant fraction of the increase in ice-sheet melt in recent years (e.g., Rignot et al. 2008). The two changes may be related, with the ice melt freshening shelf waters that are a component of these bottom waters (e.g., Jacobs & Giulivi 2010). Bottom-water salinity decreased by as much as 0.06 (on the PSS-78 scale) between 1992 and 2011 in the Ross Sea Bottom Water adjacent to the continental rise, with a smaller decrease offshore (Swift & Orsi 2012). Similar freshening occurred—again, most strongly in the newly formed bottom waters—from 1970 through 2012 offshore of the Adélie Land to the west (Katsumata et al. 2015).

Repeat hydrography has also revealed decadal variability in the salinity of the various components of the North Atlantic Deep Water (Yashayaev 2007), extending much deeper than the 2,000-m reach of Argo profiling floats, and often partly compensating for the effect of temperature variations on density (and hence sea level) in this region. The shallower anomalies are linked to variations in the strength of winter convection and Labrador Sea Water formation associated with changes in the North Atlantic Oscillation (NAO). Below 2,000 m, observed decadal changes in the deep waters fed by the Iceland-Scotland Overflow are likely linked to changes in the properties and amount of Labrador Sea Water entrained during the turbulent overflow process, whereas the observed near-bottom Denmark Strait Overflow water variations are strongly interannual.

3. CIRCULATION AND DIFFUSIVITIES

The ocean circulation moves water thousands of kilometers horizontally, carrying heat, salt, freshwater, carbon, and nutrients. Within ocean basins, these wind-driven circulations comprise the Gulf Stream and Kuroshio gyre systems of the North Atlantic and North Pacific and their counterparts in the Southern Hemisphere, namely the Brazil, Agulhas, and East Australian Current systems. The eastward-flowing Antarctic Circumpolar Current system encircles Antarctica, connecting the ocean basins and their water properties. Connected with this horizontal circulation is the ocean's overturning circulation, which involves changes in the depth and density of water parcels. Much of the change in density occurs at the surface, resulting from net heat and freshwater exchange with the atmosphere combined with vigorous vertical and lateral mixing with adjacent waters. Below the surface mixed layer, motion is approximately along surfaces of constant density (isopycnals), but slow mixing within the stratified ocean interior gradually modifies water properties, including density; on a large scale, water parcels drift across isopycnals. Because the maximum density of a water parcel tends to be close to its density when it leaves the mixed layer, the overturning circulations associated with tropical and subtropical gyres are relatively shallow. Waters below the pycnocline are ventilated from high latitudes. Deep waters are distributed globally by a horizontal circulation in which deep western boundary currents are prominent.

GO-SHIP and its predecessors are the principal source of information about changes in the shallow and deep overturning circulations. GO-SHIP observes chemical properties associated with upper-ocean ventilation (see Sections 5 and 6) and measures changes in abyssal properties and water transports (described next).

3.1. Abyssal Ocean Circulation Changes

Abyssal and deep flows are a major component of the global overturning circulation (Lumpkin & Speer 2007, Talley 2013). The deep warming discussed in Section 2.1 corresponds to a contraction rate of ~8 Sv for Antarctic Bottom Water of $\theta < 0^{\circ}$ C (Purkey & Johnson 2012). A reduction in CFC inventories in the abyssal waters of the Weddell Sea (Huhn et al. 2013) suggests a significant decrease in ventilation rates in at least that sector of the Southern Ocean.

This decline in Antarctic Bottom Water volumes (roughly a descent of $\theta = 0^{\circ}$ C at approximately 100 m decade⁻¹) appears to be associated with a reduction in northward flows of slightly warmer Lower Circumpolar Deep Water from the Southern Ocean through the South Pacific and South Atlantic (Kouketsu et al. 2011). The assimilation of repeat hydrographic section data into a general circulation model by these investigators yielded a slowdown in the northward transport of bottom waters of 0.7 Sv decade⁻¹ in the South Pacific and 0.4 Sv decade⁻¹ in the western South Atlantic from 1968 to 2005. The abyssal warming pattern in the South Pacific, with more warming at the western boundary (Sloyan et al. 2013), is consistent with a reduced eastward pressure gradient force near the bottom, and hence with reduced geostrophic northward flow. (The geostrophic balance, between the pressure gradient force and the Coriolis force, dominates ocean currents.)

In the North Pacific, an inverse model analysis using repeat hydrography data from 1985 and 2005 suggested a decrease of 1.5 Sv in northward transport of bottom waters of Southern Ocean derivation (Kouketsu et al. 2009). In the North Atlantic, analysis of five sections across 24°N occupied between 1981 and 2010 suggested that northward flow of bottom waters derived from Southern Ocean Lower Circumpolar Deep Water is reduced by order 1 Sv, although not monotonically (Frajka-Williams et al. 2011). This reduction of bottom-intensified northward flow over the Mid-Atlantic Ridge is consistent, again through geostrophic balance, with the deep pattern of warming on the western side of the Mid-Atlantic Ridge and cooling farther to the west (Johnson et al. 2008).

Whereas advection of changes in the Lower Circumpolar Deep Water in the Northern Hemisphere would take many decades, perhaps centuries, to be measurable in temperature and salinity, planetary waves can carry signatures of such changes all the way to the North Pacific in a few decades, as demonstrated by analysis of a global data assimilation of repeat hydrographic data (Masuda et al. 2010). Indeed, the highly accurate GO-SHIP measurements have shown a slight warming in very old bottom waters in the far northern Pacific (Fukasawa et al. 2004), which has been attributed to this wave mechanism.

3.2. Transport Analyses and Changes

Measuring changes in ocean circulation, and the consequences of those changes for Earth's heat and carbon budgets, is difficult; currents are highly variable on a broad range of temporal and spatial scales. Transport across hydrographic sections can be estimated using a combination of direct measurements of currents and geostrophic calculations based on the density field. More robust estimates can be made by using the hydrographic and current measurements in inverse models. GO-SHIP's synoptic, decadal sampling is complemented by data sets with more frequent sampling and with more uniform spatial coverage, such as sea surface height from satellite altimetry and Argo float velocity (e.g., Roemmich et al. 2007) or resource-intensive boundary current transport and midocean arrays (e.g., Carton & Hakkinen 2011) that provide direct velocity estimates. Ocean state estimations incorporating all of these available data sets are becoming useful circulation analysis tools (Katsumata & Masuda 2013, Wunsch & Heimbach 2013).

In the Southern Hemisphere, hydrographic section transports and properties indicate that the subtropical gyre circulations in the Indian and Pacific Oceans strengthened from the 1990s to the mid-2000s. Palmer et al. (2004) documented subtropical gyre strengthening in the Indian Ocean from 1987 to 2002 using repeats of the 32°S section. This finding was consistent with the observed signature of increased ventilation: increasing oxygen in the thermocline (McDonagh et al. 2005) and changes in upper-ocean temperature and salinity, notably in the thick mode-water layer (Bryden et al. 2003). Roemmich et al. (2007) demonstrated spin-up in the South Pacific subtropical gyre using a combination of changes in sea surface height from satellite altimetry, mid-depth velocity field from Argo floats, and thermocline pressure gradient from repeated hydrographic data, in this case from a meridional section at 170°W that showed changes in the meridional gradient of surface dynamic height and thermocline depth. The strengthening was associated with increased westerly winds and stronger Ekman convergence, corresponding with an increasing Southern Annular Mode index (Thompson et al. 2000).

As part of the deep overturn of the global circulation, the Atlantic Meridional Overturning Circulation has been of interest for several decades. For a review of the increasingly robust indications of a mild decrease in its strength, see the sidebar, The Slowing of the Atlantic Meridional Overturning Circulation.

THE SLOWING OF THE ATLANTIC MERIDIONAL OVERTURNING CIRCULATION

The Atlantic Meridional Overturning Circulation (AMOC) transports warm upper-ocean waters northward, where they are cooled in large heat-loss regions of the North Atlantic and Nordic Seas, then returned southward as cold North Atlantic Deep Water. This results in a large northward heat transport across the full length of the Atlantic. Climate models project an anthropogenic decrease in AMOC strength caused by increasing stratification in the north (Carton et al. 2014). Bryden et al. (2005) reported decreasing AMOC strength since the 1950s using hydrographic sections at 24–26°N repeated over several decades, but seasonally biased to summer. There is evidence for continued decline through 2011 (Hernández-Guerra et al. 2014). Direct measurements of the AMOC since 2004 have shown large seasonal and interannual variability but also a small decrease from 2004 to 2012 (Rayner et al. 2011, McCarthy et al. 2015) that is seen in a historical reconstruction of the AMOC from 1980 to 2005 based on data from hydrographic stations (Longworth et al. 2011). Using paleo-reconstructions, Rahmstorf et al. (2015) suggested that this recent decline is part of both decadal-scale variability and a trend going back to at least the 1930s, and likely as far back as the 1800s. Taken together, these results suggest that the AMOC is indeed slightly slowing. The meridional overturning circulation strength in the Indian and Pacific Oceans is measured by the net northward transport in the deepest layers, which therefore warms, upwells diapycnally, and returns southward at lower densities. For the meridional overturning circulation in the Southern Hemisphere Indian Ocean, the difference in transport assessed from the same 32°S 1987–2002 repeats was within the large range of uncertainty, based on geostrophic calculations from the CTD (conductivity, temperature, and depth) profiles using lowered acoustic Doppler current profiler (LADCP) velocities as an initial reference for the 2002 section (McDonagh et al. 2008).

Katsumata & Masuda (2013) used Southern Ocean repeat sections in the 1990s and 2000s and direct velocity measurements from Argo float drift in a box inverse model to estimate the Southern Ocean circulation and compare it with ocean general circulation models. They found that the meridional overturning circulation strength as measured by the northward transport of the bottom water decreased in the ocean models, which was consistent with the inverse box model, within the uncertainties. Part of the weakening is explained by the deep warming discussed in Section 3.1. By contrast, a comparison of hydrographic data from the World Ocean Circulation Experiment (WOCE) in the 1990s with those from GO-SHIP in the 2000s indicated that the transport of the eastward Antarctic Circumpolar Current has not significantly changed despite several decades of strengthening westerly winds (e.g., increase in the Southern Annular Mode index) (Katsumata & Masuda 2013).

3.3. Ocean Mixing and Vertical Diffusivity

The ocean's vertical and lateral distributions of heat, salt, and tracers are maintained not only by advection from source regions but also by ocean mixing, both across isopycnals (diapycnal) and along isopycnals. Such ocean mixing has been the focus of the Climate Variability and Predictability (CLIVAR) program's Diapycnal and Isopycnal Mixing Experiment in the Southern Ocean (DIMES) (LaCasce et al. 2014) and is not summarized here. Closing the ocean's overturning circulation requires diapycnal mixing to flux heat and buoyancy downward, reducing the density of deep waters as they gradually move upward (e.g., Munk 1966, Sloyan & Rintoul 2001, Talley 2013). Space- and time-averaged diapycnal transports associated with the ocean's large-scale overturning circulation may be diagnosed from basin-scale heat, salt, and tracer budgets using hydrographic sections, yielding estimates of diapycnal diffusivity (e.g., Ganachaud & Wunsch 2000, Lumpkin & Speer 2007, Macdonald et al. 2009, Huussen et al. 2012).

Direct observations of diapycnal diffusivity from microstructure measurements, which are scarce, have been essential for deriving a finestructure parameterization of dissipation and diffusivity (Gregg 1989, Polzin et al. 1995, Gregg et al. 2003). With this parameterization, spatial patterns of mixing can be estimated from the much more numerous CTD and LADCP profiles, such as those collected by GO-SHIP. The relationship between internal-wave shear/strain and turbulence presumes a cascade of energy from longer to shorter internal waves and turbulence (Henyey et al. 1986). In dynamically quiet regions away from boundaries and strong currents, finestructure parameterizations are accurate to within approximately a factor of two (Polzin et al. 2014, Whalen et al. 2015). Regional and global patterns of turbulence and mixing have been mapped (e.g., Naveira Garabato et al. 2004, Sloyan 2005, Kunze et al. 2006, Whalen et al. 2012).

A significant finding is that in most ocean basins the vertical distribution of diapycnal diffusivity and dissipation has two maxima (e.g., **Supplemental Figure 2**, included in **Supplemental Appendix 2** along with all subsequent supplemental figures): one in the upper ocean (200–1,000 m) and one within 1,500 m of the seafloor (Kunze et al. 2006, Huussen et al. 2012, Waterhouse et al. 2014). Diffusivities are low ($<10^{-5}$ m² s⁻²) in large regions of the ocean's thermocline. Diapycnal diffusivity is consistently high ($>10^{-4}$ m² s⁻²) over areas with rough topography, where breaking

internal waves (driven by tidal and other forces, including deep strong currents) cause turbulence, as well as in regions of high kinetic energy.

Quantitative comparisons between the diapycnal transport and observed mixing are, however, not yet satisfactory (Huussen et al. 2012). It is possible that mixing near topography has been underestimated and that, although results from the finestructure parameterization suggest enhanced vertical structure in the equatorial band, the parameterization is inaccurate because of the very different nature of internal waves and vertical shear there (Whalen et al. 2012).

These results from finestructure parameterization methods applied to temperature-salinity profile data, including those collected in GO-SHIP, are contributing to new parameterizations of mixing in global-scale ocean circulation models (Decloedt & Luther 2012, Melet et al. 2013). The structure of mixing can affect the nature of deep circulation, deep overturning, and water properties from the thermocline to the abyss, and hence accurate parameterization can affect the ability of ocean models to capture the response to changing surface forcing.

4. CARBON

4.1. Inorganic Carbon Inventories and Fluxes

The global ocean has continued to take up a substantial fraction of the C_{ant} emissions from fossil fuel combustion and net land-use change since the 1990s, and it is therefore a major mediator of global climate change. General ocean circulation models and data-constrained models suggest that the ocean absorbed approximately 37 Pg C of C_{ant} between 1994 and 2010 (Khatiwala et al. 2013) (**Figure 2**), increasing the C_{ant} inventory from 118 \pm 20 Pg C to 155 \pm 31 Pg C. This amounts to a mean uptake rate of approximately 2.3 Pg C year⁻¹, or approximately 27% of the total C_{ant} emissions over this time period. However, this globally critical estimate is based on numerical techniques using transient tracers and has not been independently verified using ocean carbon observations. The sustained repeated occupations of many of the lines measured during the 1990s and 2000s provide an observation-based uptake estimate.

Changes in dissolved inorganic carbon (DIC) concentration between repeat occupations reflect both anthropogenic C_{ant} uptake as well as natural variations in circulation and organic matter remineralization (e.g., Sabine & Tanhua 2010). Several methods have been developed and tested to accomplish this separation along repeat sections, including the extended multilinear regression method (eMLR) (Friis et al. 2005), which has recently been modified to permit basin-wide estimates of C_{ant} trends by utilizing data from repeat occupations and climatological data from *World Ocean Atlas 2013* (Locarnini et al. 2013, Zweng et al. 2013; D. Clement & N. Gruber, personal communication).

Preliminary global-scale results from this modified eMLR indicate a C_{ant} uptake rate of approximately 2.6 Pg C year⁻¹ (1994–2006), i.e., slightly above the model-based estimate of 2.3 Pg C year⁻¹ (Khatiwala et al. 2013). However, the large uncertainty of this preliminary estimate $(\pm 0.5 \text{ Pg C year}^{-1})$ precludes any statement about the significance of this difference. Using observational data and the ΔC^* method of Gruber et al. (1996), Kouketsu & Murata (2014) estimated an even higher storage rate of 2.9 \pm 0.4 Pg C year⁻¹ for the most recent decade. Takatani et al. (2014) used the GO-SHIP reference and high-frequency sections to show that the rate of C_{ant} increase on isopycnals in the western North Pacific subtropical gyre over the past two decades is consistent, within the observational uncertainty, with that expected from the atmospheric CO₂ increase, Revelle factor, and CFC age (see Section 5.1 and the reference to **Supplemental Figure 6** therein). The mean rate of C_{ant} inventory change over the past few decades varies from 0.22 \pm 0.05 mol m⁻² year⁻¹ to 0.94 \pm 0.10 mol m⁻² year⁻¹, depending on the depth to which the oceant



Compilation of 2010 column inventories (summed vertically over the full water column) of C_{ant} . Excluding the marginal seas, the global ocean inventory is 150 \pm 26 Pg C. Abbreviation: C_{ant} , anthropogenic CO₂. Figure adapted from Khatiwala et al. (2013) under the Creative Commons Attribution 3.0 license (https://creativecommons.org/licenses/by/3.0).

is ventilated. (For comparison, the 2.3–2.9 Pg C year⁻¹ global mean storage rate given above corresponds to 0.53–0.67 mol m⁻² year⁻¹.)

The C_{ant} column inventory has substantial spatial variation, with the total water column inventory in **Figure 2** dominated by upper-ocean ventilation patterns. The South Pacific has higher C_{ant} storage rates than the North Pacific (Murata et al. 2007, Sabine et al. 2008). In the Indian Ocean, C_{ant} storage rates are largest south of the equator, where C_{ant} increases have been observed to 1,800 m (Murata et al. 2010). Several studies that used observations from hydrographic sections have indicated that the Southern Ocean may be responsible for as much as 30–40% of the global C_{ant} uptake (e.g., Gruber et al. 2009, Khatiwala et al. 2009). There is still debate about whether this uptake is stored or exported (Sabine et al. 2004, van Heuven et al. 2011) and what water masses are involved (e.g., Gruber et al. 1996, Sabine et al. 2004, van Heuven et al. 2011, Pardo et al. 2014). Researchers are using both carbon parameters and other tracers (e.g., CFCs, CCl₄, and ³⁹Ar) from these cruises to investigate the possibilities. Deep western boundary currents serve as important ventilation pathways and carry an appreciable amount of anthropogenic carbon into the interior. The western basins of the North and South Atlantic and North Pacific show significantly higher C_{ant} inventories and storage rates than the eastern basins (Körtzinger et al. 1999, Murata et al. 2008, Brown et al. 2010, Waters et al. 2011).

Substantial temporal differences in C_{ant} storage rates are observed on decadal and subdecadal timescales (Sabine & Tanhua 2010; Wanninkhof et al. 2010, 2013a; Khatiwala et al. 2013; Tanhua et al. 2013a) (**Figure 3**). Similar temporal variability in C_{ant} also occurs in numerical simulations, highlighting the need to integrate repeat section occupations with other data and model information (Levine et al. 2008). Pérez et al. (2010) found that the C_{ant} storage rate in the North Atlantic was dependent on the NAO, with the highest C_{ant} storage rates occurring during positive NAO, consistent with model studies linking NAO-driven increases in mode-water formation to enhanced transport of C_{ant} from surface water into the ocean interior (Levine et al. 2011). Furthermore, Pérez et al. (2013) showed a decrease in uptake from 1990 to 2006 that they attributed to a weakening of the meridional overturning circulation.

Ocean interior carbon observations also provide a constraint on decadal average net sea-air CO_2 flux of both natural CO_2 and C_{ant} through ocean inversion procedures, provided one knows the ocean's circulation and mixing well (Gloor et al. 2003). Using an ensemble of ten general circulation models and inorganic carbon data from the 1990s and 2000s, including GO-SHIP, Gruber et al. (2009) estimated the net sea-air flux of CO_2 over 23 regions globally (**Supplemental Figure 3**). They found a remarkable level of agreement with sea-air CO_2 fluxes inferred from surface-ocean pCO_2 measurements (Takahashi et al. 2009) at a regional level, with differences rarely exceeding 0.1 Pg C year⁻¹. The C_{ant} uptake was estimated to be 2.2 \pm 0.3 Pg C year⁻¹, consistent with but slightly higher than estimates based on surface sea-air CO_2 fluxes (Takahashi et al. 2009, Wanninkhof et al. 2013b, Landschützer et al. 2014) and, independently, radiocarbon changes in the ocean interior (Graven et al. 2012).

The uptake of C_{ant} from the atmosphere into the ocean interior has also resulted in ocean acidification—a long-term decrease in pH since the beginning of the industrial era of up to 0.1 in surface waters (e.g., Feely et al. 2009). Feely et al. (2004) showed how the increased CO₂ reduced the aragonite and calcite saturation state of the global ocean. This effect of elevated atmospheric CO₂ has been illuminated by results from GO-SHIP and the earlier hydrographic sampling programs (Feely et al. 2004, 2009; Key et al. 2004; Sabine et al. 2004), showing pH changes in the surface water of approximately -0.002 year⁻¹ from 1991 to 2006 along sections in the North Pacific (for a summary, see Rhein et al. 2013). The Global Ocean Data Analysis Project (GLODAP) data product included estimates of the preindustrial DIC concentration derived from

differences between the measured DIC and the estimated anthropogenic component. Orr et al. (2005) used these GLODAP estimates for comparison with 13 models in the Ocean-Cycle Model Intercomparison Project (OCMIP-2) to show the anthropogenic reduction in aragonite and calcite saturation, and then as a baseline for 100-year projections in 3 coupled models forced with several Intergovernmental Panel on Climate Change (IPCC) scenarios for rising atmospheric CO₂. Yool



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et al. (2013a,b) used GLODAP and *World Ocean Atlas 2005* (Antonov et al. 2006, Locarnini et al. 2006) data products to estimate the pH change from the preindustrial to the present (**Supplemental Figure 4**). The smallest pH changes (-0.04 to -0.06) have been in the tropics and subtropics; the greatest (-0.08 to -0.1) have been in the northern North Atlantic and North Pacific and in a circumpolar band in the Southern Ocean. The larger changes result from a combination of greater C_{ant} invasion, lower buffer capacity, and lower water temperature (Sabine et al. 2004, Feely et al. 2009, Egleston et al. 2010).

4.2. Dissolved Organic Carbon

Dissolved organic carbon (DOC) is one of the largest bioreactive pools of carbon in the ocean (Hansell et al. 2009, 2012). Over the past decade, time-series and basin-scale observations (~50,000 data points) have revealed temporal and spatial variability of DOC in unprecedented detail (**Figure 4**); from this detail, the processes controlling the variability can be inferred. The inventory of oceanic DOC is estimated to be ~662 \pm 32 Pg C, 200 times the mass of the organic carbon in suspended particles but approximately 1/50th of the total DIC inventory (Hansell et al. 2009).

The bulk DOC pool contains a myriad of compounds that turn over on timescales from seconds to millennia (Hansell et al. 2012, Carlson & Hansell 2015). The majority of the newly produced DOC is rapidly remineralized by heterotrophic bacterioplankton within the ocean's surface layer (Carlson & Hansell 2015). However, ~20% of global net community production (~1.9 Pg C year⁻¹) escapes rapid microbial degradation for periods long enough to be exported from the euphotic zone via convective mixing or isopycnal exchange into the ocean's interior (Copin-Montgut & Avril 1993, Carlson et al. 1994, Hansell et al. 2009). DOC export occurs with deep- and mode-water formation in the North Atlantic (**Figure 4**) as midlatitude, warm, DOC-enriched surface waters are transported with surface currents to subpolar and high latitudes. Here, convective overturn transports the DOC deep into the interior, where it is slowly removed through southward flow.

Previously, estimating the removal rates of exported DOC within the ocean's interior was not possible owing to the slow decay rates of the biologically recalcitrant DOC. However, coupled measures of bulk DOC, DOC characterization, water-mass age tracers, and other biogeochemical variables (Hansell et al. 2009, 2012; Carlson et al. 2010; Goldberg et al. 2011) obtained by GO-SHIP have greatly improved understanding of bulk DOC distribution, fractions of DOC lability, and DOC export (Hansell et al. 2012, Hansell 2013). For example, linear and multiple linear regression models applied to pairwise measurements of DOC and CFC-12 ventilation age retrieved from major water masses within the main thermocline and North Atlantic Deep Water (lines A16, A20, and A22) allow estimates of decay rates for exported DOC ranging from 0.13 to 0.94 μ mol kg⁻¹ year⁻¹, with higher DOC concentrations driving higher rates. A comparison of the change in DOC with the change in oxygen in the same water masses suggested that DOC

Figure 3

Decadal storage rates of C_{ant} as observed from repeat hydrography cruises. (*Left column*) Measurement intervals bracketed by repeat hydrography cruises in the Northern Hemisphere (*solid lines*), tropics (*dasb-dotted lines*), and Southern Hemisphere (*dasbed lines*); each color denotes a different study. Estimates of uncertainties are shown as vertical bars with matching colors along the right axes. The solid black lines represent the basin average storage rates using Green's functions. (*Right column*) Maps of decadal storage rates from a Green's function inversion averaged over 1980–2005 using data shown in the left column; note that the color scales differ in each subpanel. Abbreviation: C_{ant} , anthropogenic CO₂. Figure adapted from Khatiwala et al. (2013) under the Creative Commons Attribution 3.0 license (https://creativecommons.org/licenses/by/3.0).







Distributions of DOC in the Atlantic, Pacific, and Indian Oceans on GO-SHIP repeat hydrography lines A16, P16, and I8/I9, respectively, with water from all lines connected via the Antarctic Circumpolar Current. Arrows depict water-mass renewal and circulation; white lines indicate isopycnal surfaces. Note the DOC export in the North Atlantic with North Atlantic Deep Water formation and the subsequent DOC loss during deep circulation to the South Atlantic. In the Pacific, there is a northward invasion of relatively DOC-enriched Circumpolar Deep Water along the bottom, slow removal of DOC into the far North Pacific, and return flow of DOC-impoverished water to the south at mid-depths. Abbreviations: AABW, Antarctic Bottom Water; AAIW, Antarctic Intermediate Water; CDW, Circumpolar Deep Water; DOC, dissolved organic carbon; GO-SHIP, Global Ocean Ship-Based Hydrographic Investigations Program; IODW, Indian Ocean Deep Water; IOIW, Indian Ocean Intermediate Water; LCDW, Lower Circumpolar Deep Water; NADW, North Atlantic Deep Water; PDW, Pacific Deep Water; SAMW, Subantarctic Mode Water. Figure adapted from figure 2 in Hansell et al. (2009).

oxidation contributes 5–29% of the apparent oxygen utilization in the deep water masses of the North Atlantic (Arístegui et al. 2002, Carlson et al. 2010).

Measurements of carbohydrate and dissolved combined neutral sugar concentrations allow further assessment of changes in chemical character along meridional transects in the North Atlantic (A20) and South Pacific (P16S). As microbes remineralize dissolved organic matter (DOM), they preferentially remove the most labile components of DOM, such as carbohydrates and dissolved combined neutral sugars, leaving behind more recalcitrant components. Survey data of these components demonstrate systematic diagenetic patterns across ocean basins (Goldberg et al. 2011), providing further insight into the roles that stratification, ventilation, export, and subsequent remineralization play in DOM quality. For example, meridional transects in the South Pacific and North Atlantic reveal a common diagenetic trajectory in the surface 300 m along which glucose becomes enriched relative to mannose and galactose as DOM is degraded. Departure from this trajectory within the euphotic zone could indicate recently produced "bloom" DOM, whereas departure in the mesopelagic zone could indicate recently exported DOM (Goldberg et al. 2011). The compositional data together with bulk DOM dynamics provide important information about DOM production, consumption, and transformation.

5. OCEAN VENTILATION: TRANSIENT TRACERS

5.1. Chlorofluorocarbons, SF₆, and Tritium-³He

Anthropogenic transient-tracer distributions provide insight into the pathways, rates, and temporal variations in the processes ventilating the ocean on decadal timescales (Johnson et al. 2008, Wanninkhof et al. 2013b). CFCs, sulfur hexafluoride (SF₆), and bomb tritium have been entering the ocean since the middle of the twentieth century (**Supplemental Figure 5**), during which time the ocean has taken up approximately two-thirds of its anthropogenic carbon inventory. CFC and tritium-³He data, especially as used with transit time distributions (TTDs; see below), have played a key role in reconstructing the complex spatial and temporal evolution of C_{ant} in the global ocean (Tanhua et al. 2008, Khatiwala et al. 2009, Sabine & Tanhua 2010, Wanninkhof et al. 2013a), estimating apparent oxygen utilization rates (Jenkins 1977; Stanley et al. 2012; Sonnerup et al. 2013, 2015), and separating observed changes in oxygen and nutrients into physical (e.g., solubility, circulation, and mixing) and biological processes (Jenkins 1998; Emerson et al. 2001; Mecking et al. 2006; Sonnerup et al. 2013, 2015). Transient tracers have also been used in testing and evaluating a variety of global ocean circulation and biogeochemical models (Dutay et al. 2002, Matsumoto et al. 2004, Peacock et al. 2005, Hartin et al. 2014, Long et al. 2013).

Ventilation rates of a water mass can be estimated using transient-tracer-derived ages, which measure the elapsed time since last contact with the surface ocean (see global age maps in **Supplemental Figure 6**). The well-characterized atmospheric histories of the CFCs and SF₆ (Walker et al. 2000, Bullister 2015) along with the solubility of these gases in seawater (Warner & Weiss 1985, Bullister et al. 2002) allow the equilibrium concentrations of these compounds in the surface ocean, and thus newly subducted waters, to be modeled as a function of time (e.g., Tanhua et al. 2013b). The Montreal Protocol on Substances that Deplete the Ozone Layer restricted the production and uses of CFCs beginning in 1989, which resulted in atmospheric CFC-11 and CFC-12 concentrations peaking in the late 1990s and early 2000s, respectively, and then slowly decreasing, whereas SF₆ has been increasing in the atmosphere at 5-7% per year for the past two to three decades (**Supplemental Figure 5**). Decay of tritium to ³He provides an additional radioisotope natural clock for the isolation of water parcels from the atmosphere (Jenkins 1977).

Tracer ages are modified by mixing and complicated by the nonlinear source functions (e.g., Doney et al. 1997, Mecking et al. 2006, Tanhua et al. 2013b, Waugh et al. 2013). A commonly used technique, TTDs, assumes that the tracer age is composed of a spectrum of ages. The addition of SF₆ provides improved estimates of mixing of different water parcels. Two TTD methods have been used: the inverse Gaussian method, which assumes a one-dimensional advection-diffusion process (e.g., Waugh et al. 2003, 2013), and the maximum entropy method, which relaxes this assumption and provides information on water-mass composition as well as ages (Holzer et al. 2010). Both methods can include natural radiocarbon (¹⁴C), which provides temporal information for water formed prior to the transient-tracer invasion (see Section 5.2).

💫 Supplemental Material

The global thermocline is well ventilated on the timescale of the CFC/SF₆ and bomb-tritium transient, whereas deeper isopycnal surfaces are much less ventilated (**Figure 5**, **Supplemental Figure 6**). The CFC-12 decadal differences shown in **Figure 5** illustrate the invasion of the time-dependent signal into the thermocline, with the greatest increases at the front of the pulse of the tracer. Regions of the ocean where *p*CFC ages in the thermocline exceed several decades include the deep portions of oxygen minimum zones and the northern Indian Ocean thermocline. CFC distributions, as presented in the WOCE Hydrographic Program Atlases, reveal well-ventilated deep and bottom waters in the Southern Ocean (Sparrow et al. 2005–2013) and North Atlantic (LeBel et al. 2008).

Models of climate change predict that increased stratification should lead to decreased ventilation. Such an effect is seen in the Northern Hemisphere subtropics and subpolar thermoclines and in the Antarctic Circumpolar Current, where predicted CFCs based on TTDs were lower than expected and oxygen declined (**Figure 5**). However, decadal trends in the subtropical gyres of the Southern Hemisphere indicate increased ventilation for the deep thermocline. The observed increase in CFC-11 and CFC-12 concentrations in the Southern Hemisphere subtropical thermocline compared with those in the 1990s (**Figure 5**) has been greater than predicted by either models or TTDs, and tracer ages have decreased (Fine 2011, Waugh et al. 2013, Fine et al. 2014) (**Figure 5**). Thermocline oxygen increases (McDonagh et al. 2005, Talley 2009, Mecking et al. 2012) (see Section 6.1 and the reference to **Supplemental Figure 9** therein) have been associated with increasing ventilation caused by changes in the Southern Annular Mode (Roemmich et al. 2007) that were reflected in increasing CFC concentrations in the lower thermocline (Fine 2011). Both oxygen distributions and TTDs lead to the same conclusion: that ventilation rates in the southern subtropical gyres had been increasing into the 2000s, but this trend has reversed in recent years (see Section 6.1).

Transient-tracer inventory calculations (Smethie & Fine 2001, Orsi et al. 2002, Rhein et al. 2002, Smethie et al. 2007, LeBel et al. 2008) provide integral water-mass formation rates for deep water masses (Hall et al. 2007). As an example, North Atlantic CFC-12 inventory changes over the period 1997–2005 showed a reduction in classical Labrador Sea Water formation (Rhein et al. 2011), whereas upper Labrador Sea Water formation increased (Kieke et al. 2006, 2007). Altimeter analysis showed that decreased classical Labrador Sea Water formation was accompanied by a decreased subpolar gyre transport index (Curry & McCartney 2001, Kieke et al. 2007, Rhein et al. 2011) and decreased strength of the subpolar gyre (Hakkinen & Rhines 2004, Hakkinen et al. 2008). Measurements of CFCs confirm the importance of the deep western boundary current as an advective pathway into the subtropics, and interior CFC concentrations support the importance of interior pathways that are related to the role of eddies and winds (Lozier 2010). This is consistent with tritium-³He data from the Transient Tracers in the Ocean program in the North Atlantic's deep western boundary current compared with the deep-interior basins east of this current (Doney & Jenkins 1994).

5.2. Radiocarbon

Oceanic ¹⁴C is both a transient and a natural tracer that has undergone decadal changes owing to atmospheric nuclear weapons testing in the 1950s and 1960s. The bomb spike doubled the atmospheric ¹⁴C level, an increase that was large enough to be easily measured as it moved into the upper ocean and finally toward the abyss. Like C_{ant} , the distribution of bomb-produced ¹⁴C varies relative to a background of natural ¹⁴C. Improved measurement technology has reduced sample-size requirements by a factor of 1,000 relative to the initial high-quality survey (performed in the mid-1970s), and measurement precision has improved by a factor of 2. Key et al. (2004)



(*a,b*) Differences in oxygen (panel *a*) and CFC-11 (panel *b*) between 0 and 1,500 m along three transects: A16 in the Atlantic Ocean along ~20°W (*top*, 2005–2006 minus 1989), 18/19 in the Indian Ocean along ~95°E (*middle*, 2005 minus 1995), and P16 in the Pacific Ocean along ~150°W (*bottom*, 2005–2006 minus 1991). **Supplemental Figure 1** provides a map of the complete A16, 18/19, and P16 section locations. Properties were interpolated to neutral density surfaces, differenced, and then projected back to depth coordinates, using the neutral density from the earlier year for the projection. Thus, the heave caused by vertical migration of the neutral density surfaces is excluded. Each panel includes overlain contours of neutral density (*red lines*) and of the property itself from the earlier occupation (*black lines*). (*c*) Differences between TTD-predicted and observed *p*CFC-12 for the 2005 cruises compared with those from 1989 (line A16, *top*) and 1991 (line P16, *bottom*). Isopycnals (*black lines*) are from earlier occupations of the A16 and P16 sections. The TTD calculations use $\Delta/\Gamma = 1.0$ and a surface saturation of 90%. Negative values (*blues* and *purples*) mean that there was a higher *p*CFC-12 than expected in the 2005 occupation, indicating younger water or greater ventilation than expected; positive values (*yellows* and *reds*) mean that there was a lower *p*CFC-12 than expected in the 2005 occupation, so from the 2005 occupation, indicating younger water or greater ventilation than expected; positive values (*yellows* and *reds*) mean that there was a lower *p*CFC-12 than expected in the 2005 occupation, indicating older water or less ventilation than expected. The red lines in the middle subpanel indicate the locations of the PF and SAF from Orsi et al. (1995). Abbreviations: CFC, chlorofluorocarbon; PF, polar front; SAF, subantarctic front; TTD, transit time distribution; WOCE, World Ocean Circulation Experiment. Panel *c* adapted from Waugh et al. (2013).



Changes in bomb-produced radiocarbon (Δ^{14} C) on potential density σ_{θ} surfaces for two transects: (*a*) P16 in the Pacific along ~150°W (2005–2006 minus 1991) and (*b*) A16S in the South Atlantic along ~20°W (2005–2006 minus 1989). In the left subpanels, negative values (*shades of blue*) indicate a reduction in Δ^{14} C, and positive values (*shades of red*) indicate an increase in Δ^{14} C. The right panels show the zonally averaged differences as a function of potential density. Figure adapted from Graven et al. (2012).

produced the first global three-dimensional maps of the distribution of measured, background, and bomb-produced ¹⁴C, which were then integrated to yield inventories. The GO-SHIP sections from the 2000s have extended the time series, have been incorporated into GLODAPv2 (Olsen et al. 2014, 2015; Key et al. 2015), and have allowed bomb-produced ¹⁴C to be monitored as it is mixed into the ocean (**Figure 6, Supplemental Figures 7** and **8**).

Maps and inventories of ¹⁴C have been used to determine global mean air-sea exchange rates for CO₂ (Naegler et al. 2006, Sweeney et al. 2007), calibrate global ocean general circulation models, and determine ocean ventilation rates (Matsumoto et al. 2004). More recently, Graven et al. (2012) have demonstrated that the temporal changes in ocean interior Δ^{14} C provide important independent constraints on the oceanic uptake of C_{ant}, substantiating a rate between 1.7 and 2.3 Pg C year⁻¹ (see Section 4.1). This is because in recent decades, the oceanic uptake of ¹⁴C (**Figure 6**) has been controlled largely by ocean circulation and mixing rather than by air-sea gas exchange, as was the case in the early decades after the bomb spike.

6. OCEAN VENTILATION: OXYGEN AND NUTRIENTS

6.1. Oxygen

Large and systematic changes in oxygen, mostly reductions, have been documented over the last two decades through GO-SHIP repeat hydrography and local station time series (e.g., Keeling et al. 2010). The oxygen changes indicate large-scale changes in ventilation, temperature (as it impacts oxygen solubility), and possibly remineralization (which can impact ecosystem health) (Deutsch et al. 2015). Some of the observed oxygen changes could be due to changes in biology, but based on modeling studies (Deutsch et al. 2005) and correlations with physical forcing such as the NAO (Johnson & Gruber 2007), the consensus is that physical changes usually predominate. The combination of oxygen data with transient-tracer data provides further evidence regarding the timescales at which the ventilation changes occur (see Section 5.2). The combination of oxygen data with carbon data (e.g., Sabine et al. 2008) and pH data (e.g., Byrne et al. 2010) has allowed separation of DIC/pH changes along repeat sections into anthropogenic and ventilation/remineralization components, including their respective effects on carbon storage and ocean acidification.

The deoxygenation in the open-ocean thermocline over the past two decades is consistent with the expectation that warmer waters will hold less dissolved oxygen (the solubility effect) and that warming-induced stratification leads to a decrease in the transport of dissolved oxygen from surface to subsurface waters (the stratification effect) (Matear & Hirst 2003, Deutsch et al. 2005, Frölicher et al. 2009). Approximately 15% of the oxygen decline between 1970 and 1990 can be explained by warming, and the remainder can be explained by increased stratification (Helm et al. 2011).

Oxygen decline is found most consistently in the oxygen minimum zones of the tropical Pacific, Atlantic, and Indian Oceans and in the subpolar and subtropical North Pacific and North Atlantic (Johnson & Gruber 2007; Keeling et al. 2010; Stramma et al. 2010, 2012; Keeling & Manning 2014). Differences between GO-SHIP and WOCE oxygen measurements on midocean meridional sections show these Northern Hemisphere declines as well as a decline within the Antarctic Circumpolar Current thermocline in the far south, as found by Aoki et al. (2005) (**Figure 5**).

Analyses in the North Atlantic over more than 50 years paint a more varied picture. Although the upper, mode, and intermediate waters are indeed losing oxygen because of changes in solubility, the deeper waters actually gained oxygen over this period owing to changes in circulation and ventilation (Stendardo & Gruber 2012). The trend in the North Pacific is based on a >50-year time series of oxygen data at Ocean Station P, which shows large bidecadal cycles on top of the smaller long-term trend ($0.39-0.70 \mu$ mol kg⁻¹ year⁻¹; Whitney et al. 2007), and on an ~30-year time series in the Oyashio off northern Japan, which also shows large bidecadal cycles on top of the long-term trend ($0.9 \pm 0.5 \mu$ mol kg⁻¹ year⁻¹; Ono et al. 2001). The North Pacific GO-SHIP cruises have been instrumental in determining the spatial extent of the decadal-scale variations that extend into the subtropics in the east (e.g., Emerson et al. 2004, Mecking et al. 2008) and west (Kouketsu et al. 2010, Takatani et al. 2012, Sasano et al. 2015).

In contrast to the oxygen declines in many regions, oxygen in the subtropical Southern Hemisphere thermocline increased over the past few decades (**Figure 5**, **Supplemental Figure 9**). At 32°S in the Indian Ocean, McDonagh et al. (2005) found a substantial increase in oxygen from 1987 to 2002, reversing an oxygen decline observed earlier (Bindoff & McDougall 2000). An oxygen increase also occurred over similar time periods along the 30°S repeat sections in the Pacific and Atlantic (Talley 2009). This oxygenation of the subtropical thermocline likely resulted from increased ventilation caused by spin-up of the Southern Hemisphere gyres (see Sections 3.2

🜔 Supplemental Material

and 5.1), documented at least for the Pacific based on dynamic height changes (Roemmich et al. 2007). The most recent 2009 repeat of the I5 section, however, indicates yet another reversal in gyre conditions, with oxygen decreasing (Mecking et al. 2012) (**Supplemental Figure 9**) in response to natural decadal variability as well as anthropogenic climate change (Kobayashi et al. 2012).

6.2. Nutrients

Nutrient-based geochemical studies have greatly increased understanding of basin-scale processes governing nutrients and oxygen. A linear combination of nitrate and phosphate, defined as N*, provides an estimate of excess nitrogen (e.g., from nitrogen fixation or atmospheric deposition) or nitrogen deficit (e.g., from denitrification or anammox) relative to global Redfield stoichiometry and is widely used for mapping the nitrogen cycle (**Supplemental Figure 10**). Use of N* has contributed to an upward revision of global estimates of nitrogen fixation (Moore & Doney 2007). Another geochemical tracer, Si*, representing the difference between silicic acid and nitrate concentrations, has shown the importance of Southern Ocean nutrient supply to the global thermocline north of 30°S (Sarmiento et al. 2004).

Nutrient changes observed over the past several decades have been attributed to (*a*) physical stratification and wind changes that also affect oxygen (see Section 6.1) and (*b*) human activities, mainly fossil fuel combustion and fertilizer production, that have increased atmospheric deposition and riverine discharge of nitrate to the ocean, thereby impacting the ocean biological carbon pump (Doney 2010). Over the past several decades, Whitney et al. (2013) have observed decreasing oxygen and increasing nutrients below the pycnocline in the subarctic Pacific, forced by changes in the advective flux of oxygen and nutrients, surface production and export, and remineralization. Interestingly, the vertical flux of nutrients to the euphotic zone remained relatively stable because increasing nutrient concentrations below the pycnocline offset an increase in pycnocline stratification. The long-term trends can be obscured by large interannual and multidecadal fluctuations in upper-ocean nutrient distributions that are coupled with climate modes of variability (Di Lorenzo et al. 2009, Henson et al. 2010).

In terms of human activities, Kim et al. (2014) used N* measurements and CFC-based ventilation rates to determine that atmospheric deposition of anthropogenic nitrate in the western North Pacific has been associated with increasing excess nitrate in the upper water column over the last 30 years. The effect was highest close to Asia, a source region for reactive nitrate, with rates decreasing eastward across the North Pacific. This input may eventually transform this ecosystem from nitrate to phosphate limitation (Kim et al. 2014). In the North Atlantic subtropical gyre, rates of atmospheric nitrate deposition are comparable to estimated rates of N₂ fixation, but reactive nitrate is rapidly consumed and does not accumulate in surface waters (Zamora et al. 2010). Instead, excess nitrate is accumulating in the main thermocline, with ~15–20% attributable to atmospheric deposition (Hansell et al. 2007, Zamora et al. 2010).

Detection of long-term climate trends in the presence of natural variability and current nutrient data uncertainty will require many decades of sustained observation and improved measurement accuracy during GO-SHIP cruises. Utilization of historical nutrient data to assess decadal trends in the oceans has been hindered by their inaccuracy, manifested as offsets in deepwater concentrations measured by different laboratories (Zhang et al. 2000). At present, development of Certified Reference Materials for seawater nutrient measurement is under way, and their widespread use in shipboard measurements in conjunction with unified methodology and instrumentation will improve the internal consistency of the global nutrient data set generated in GO-SHIP (Natl. Res. Counc. 2002).

SUMMARY POINTS

- 1. The ocean is warming, taking up the majority of the excess heat in the Earth system over recent decades; approximately 19% of this heat is below 2,000 m.
- 2. Abyssal waters originating in the Southern Ocean have been warming; those from the Pacific and Indian Ocean sectors have also been freshening.
- 3. In many regions, vertical diffusivity increases from a minimum in the thermocline to a maximum within the bottom 1,500 m.
- 4. Increased stratification has resulted in a decline in oxygen and increase in nutrients in the Northern Hemisphere thermocline and an expansion of the tropical oxygen minimum zones. Southern Hemisphere thermocline oxygen increased in the 2000s owing to stronger wind forcing that increased the ventilation of the subtropical gyres, as supported by evidence from transient-tracer changes.
- 5. Anthropogenic carbon uptake has been quantified and mapped, with supporting evidence from transient tracers including chlorofluorocarbons (CFCs) and radiocarbon; the oceans currently sequester approximately 27% of the anthropogenic carbon released to the atmosphere by fossil fuel burning and land-use change.
- 6. As anthropogenic CO_2 invades the ocean, the upper ocean is acidifying.
- 7. Dissolved organic carbon, a large, bioactive reservoir, has been mapped and inventoried for the first time, and its contribution to export production (\sim 20%) and deep-ocean oxygen utilization have been quantified.
- 8. Atmospheric and riverine inputs of anthropogenic nutrients have changed the ocean biogeochemistry in the upper waters of the western North Pacific and the thermocline of the North Atlantic.

FUTURE ISSUES

- 1. Sustaining the ship-based, full-depth ocean observations coordinated through GO-SHIP is of high priority, particularly because we anticipate accelerating changes in the coming decades.
- 2. GO-SHIP evolves with experience and with new technology. We look forward to incorporating advances in biological and biogeochemical sensing techniques that will expand the role of GO-SHIP in documenting long-term changes in marine biogeochemistry and ecosystems.

DISCLOSURE STATEMENT

B.M. Sloyan and R. Wanninkhof are co-chairs and M. Kramp is project coordinator of the international GO-SHIP program. L.D. Talley, R.A. Feely, and G.C. Johnson are co-chairs of the US GO-SHIP program. C.A. Carlson is co-editor and R.A. Fine is a member of the Editorial Committee of the *Annual Review of Marine Science*. All authors have received funding related to the program results reported in this review.

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