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**Correspondence** and requests for materials should be addressed to T.V. (e-mail: tvogt@bnl.gov).

## A short-term sink for atmospheric CO<sub>2</sub> in subtropical mode water of the North Atlantic Ocean

Nicholas R. Bates\*, A. Christine Pequignet\*, Rodney J. Johnson\* & Nicolas Gruber†

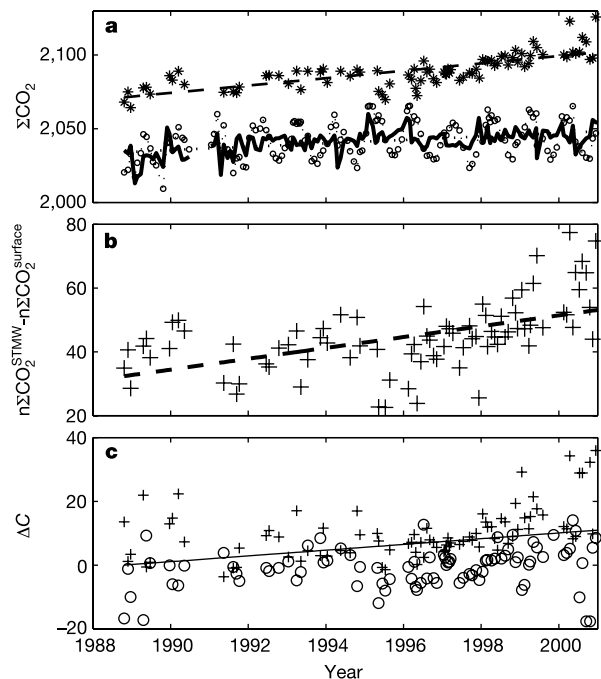
\* Bermuda Biological Station For Research, Inc., Ferry Reach, Bermuda, GE01  
 † University of California at Los Angeles, Los Angeles, California 90095-4996, USA

Large-scale features of ocean circulation, such as deep water formation in the northern North Atlantic Ocean<sup>1</sup>, are known to regulate the long-term physical uptake of CO<sub>2</sub> from the atmosphere by moving CO<sub>2</sub>-laden surface waters into the deep ocean. But the importance of CO<sub>2</sub> uptake into water masses that ventilate shallower ocean depths, such as subtropical mode waters<sup>2</sup> of the subtropical gyres, are poorly quantified. Here we report that, between 1988 and 2001, dissolved CO<sub>2</sub> concentrations in subtropical mode waters of the North Atlantic have increased at a rate twice that expected from these waters keeping in equilibrium with increasing atmospheric CO<sub>2</sub>. This accounts for an extra ~0.4–2.8 Pg C (1 Pg = 10<sup>15</sup> g) over this period (that is, about 0.03–0.24 Pg C yr<sup>-1</sup>), equivalent to ~3–10% of the current net annual ocean uptake of CO<sub>2</sub> (ref. 3). We suggest that the lack of strong winter mixing events, to greater than 300 m in depth, in recent decades is responsible for this accumulation, which would otherwise disturb the mode water layer and liberate accumulated CO<sub>2</sub> back to the atmosphere. However, future climate variability (which influences subtropical mode water formation<sup>1,4–8</sup>) and changes in the North Atlantic Oscillation<sup>9</sup> (leading to a return of deep winter mixing events) may reduce CO<sub>2</sub> accumulation in subtropical mode waters. We therefore conclude that, although CO<sub>2</sub> uptake by subtropical mode waters in the North Atlantic—and possibly elsewhere—does not always represent a long-term CO<sub>2</sub> sink, the phenomenon is likely to contribute substantially to interannual variability in oceanic CO<sub>2</sub> uptake<sup>3</sup>.

The net global ocean exchange of CO<sub>2</sub> between the ocean and the atmosphere depends on the rates of CO<sub>2</sub> flux across the air–sea interface, and the supply of CO<sub>2</sub> to (and its removal from) the ocean mixed layer. The transfer of CO<sub>2</sub> from the ocean mixed layer to deeper depths is a complex function of biological and physical processes that operate over a wide range of timescales (<1 to >1,000 yr). In subpolar/polar regions, the formation and subsequent sinking of intermediate and deep waters represent a physical mechanism for transporting CO<sub>2</sub> from the surface to the deep ocean. In the subtropical gyres, the shallow depths between the seasonal and main thermoclines are ventilated as a result of the formation of subtropical mode waters (STMWs)<sup>2</sup>. However, the

rates and interannual variability in the uptake of CO<sub>2</sub> from the atmosphere into STMW and the fate of this CO<sub>2</sub> are poorly quantified at present.

The STMW of the North Atlantic Ocean is formed each winter by cooling and convective mixing at the northern edges of the subtropical gyre south of the Gulf Stream<sup>3–5</sup>. The shallow depths of this gyre (~250–400 m)<sup>4,10</sup> are ventilated during STMW formation. The STMW layer is found throughout the subtropical gyre, and its age increases following the mean geostrophic circulation from the site of STMW formation to the western boundary current<sup>11</sup>. This water mass is classically defined by temperatures ranging from 17.8 to 18.4 °C (ref. 4), by a salinity of ~36.5 ± 0.05, and by a minimum in the vertical gradient of potential density (or isopycnic potential vorticity)<sup>2,5,7,12</sup>. The strength and geographic extent of STMW formation is highly variable interannually<sup>4,5,10,13</sup>, and primarily coupled to North Atlantic Oscillation (NAO)<sup>1,4,5,8,13</sup> variability—the NAO being a dipole meridional oscillation in atmospheric pressure between the Iceland Low and the Azores High<sup>9</sup>. Observations of STMW variability date back to 1954 with time-series hydrographic data collected at the Hydrostation S site (32° 10' N, 64° 30' W) near Bermuda<sup>6,12–14</sup>, expendable bathythermograph (XBT) surveys since the 1960s<sup>4,7</sup>, and monthly sampling since 1988 at the US Joint Global Ocean Flux Study (JGOFS) Bermuda Atlantic Time-series Study (BATS) site (31° 50' N, 64° 10' W) near Bermuda<sup>15</sup>.



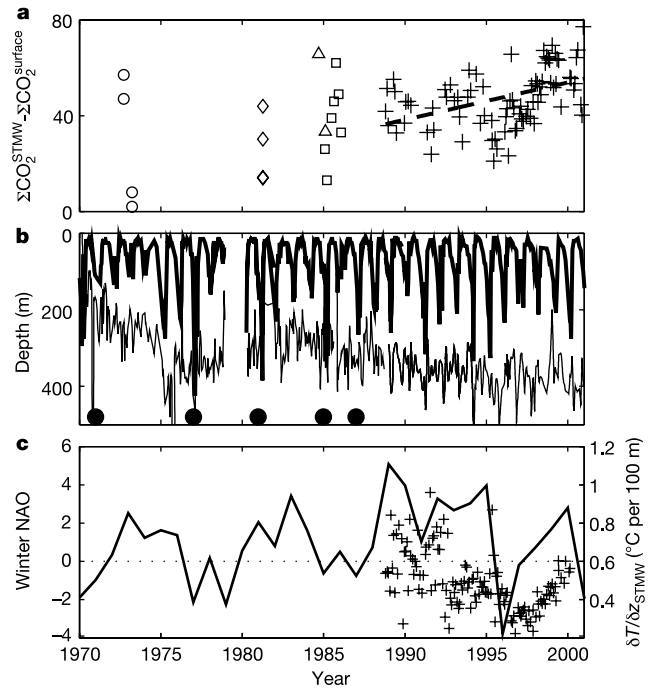
**Figure 1** Interannual variability and trends of  $\Sigma\text{CO}_2$  and hydrography in the western North Atlantic near Bermuda (1988–2001). **a**, Trends of surface  $\Sigma\text{CO}_2$  (open circles) and STMW  $\Sigma\text{CO}_2$  (asterisks) sampled at BATS from October 1988 to September 2001. Surface-layer  $\Sigma\text{CO}_2$  data were normalized to the mean salinity of 36.6. Also shown are seasonally adjusted surface layer  $\Sigma\text{CO}_2$  data, where the cyclo-stationary seasonal cycle has been removed by fitting harmonic functions of time with periods of 12, 6 and 4 months to the data. Regression lines are shown for the STMW layer (dashed line) and the surface layer (solid line). **b**, Difference between surface-layer and STMW  $\Sigma\text{CO}_2$  sampled at BATS from October 1988 to September 2001. Both surface and STMW data have been adjusted to account for the cyclo-stationary seasonal cycle. The dashed line is the linear regression of the data. **c**, Long-term trends of  $C_{\text{anti}}$  (regression line), the gas exchange component  $C_{\text{gasex}}$  ('plus' symbols), and the biological component  $C_{\text{bio}}$  (open circles) in the STMW layer. Details and regression statistics are given in Table 1.  $n\Sigma\text{CO}_2$ ,  $\Sigma\text{CO}_2$  and  $\Delta C$  units are  $\mu\text{mol kg}^{-1}$ .

Ocean inorganic carbon data have been collected at the BATS site each month since 1988. Water-column seawater samples from 158 cruises were analysed for total carbon dioxide ( $\Sigma\text{CO}_2$ ) content by gas extraction and coulometric methods<sup>15,16</sup>. Highly precise and accurate measurements of  $\Sigma\text{CO}_2$ , a requisite for determining long-term trends, have been achieved by analysing seawater certified reference materials over time<sup>15,16</sup>.  $\Sigma\text{CO}_2$  samples for near-surface waters only have been collected at Hydrostation S since 1983<sup>17</sup> and, unfortunately, do not provide comparative information about STMW  $\text{CO}_2$  variability before 1988.

Long-term observations at the BATS site indicate that the  $\Sigma\text{CO}_2$  concentrations of surface waters and of the STMW layer have increased at divergent rates over time ( $dC/dt$ ) since sampling began in 1988. In the surface layer, the mean rate of increase of  $n\Sigma\text{CO}_2$  ( $\Sigma\text{CO}_2$  normalized to a constant salinity to account for the dilution/concentration effect of freshwater addition/removal) is  $1.25 \pm 0.14 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (see Methods) (Fig. 1a; Table 1) The rate of change of surface ocean  $\Sigma\text{CO}_2$  in the western North Atlantic is thus similar to that observed in the subtropical gyre of the North Pacific Ocean ( $1.18 \pm 0.32 \mu\text{mol kg}^{-1} \text{CO}_2 \text{yr}^{-1}$ )<sup>18</sup>. In STMW, however, the mean rate of change of  $\Sigma\text{CO}_2$  is much higher, increasing at  $2.64 \pm 0.26 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (using a 17.8–18.4 °C temperature criterion to define STMW; Fig. 1a, Table 1). This result is independent of the criterion used to define the STMW layer, as we find a very similar rate of change of  $2.22 \pm 0.27 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (Table 1) if we use a density criterion (that is, 26.4  $\sigma_\theta$  isopycnal surface).

These long-term trends indicate that the subtropical gyre of the North Atlantic is at present acting as a significant and detectable sink for anthropogenic  $\text{CO}_2$ . From 1988 to 2001,  $\Sigma\text{CO}_2$  has increased in the surface layer and STMW by  $\sim 15$  ( $\sim 0.8\%$ ) and  $\sim 33 \mu\text{mol kg}^{-1}$  ( $\sim 1.5\%$ ), respectively, while the vertical difference (that is, difference between surface and STMW  $\text{TCO}_2$ , or  $\delta_2C$ ) has increased from  $\sim 35$  to  $\sim 55 \mu\text{mol kg}^{-1}$  (Fig. 1b). Before 1988, the mean vertical difference in  $\Sigma\text{CO}_2$  between surface and STMW, determined from  $\Sigma\text{CO}_2$  data from a few stations in the Sargasso Sea during the 1972–86 period, was  $\sim 34 \mu\text{mol kg}^{-1}$  (Fig. 2a). The

vertical difference in  $\Sigma\text{CO}_2$  should remain fairly constant over time if the physical and biological processes that influence the  $\Sigma\text{CO}_2$  contents of the subtropical gyre were in steady state and the ocean was just accumulating anthropogenic  $\text{CO}_2$  in response to the increasing atmospheric  $\text{CO}_2$  concentrations. However, the large changes in  $\delta_2C$  and in the  $\Sigma\text{CO}_2$  contents of the STMW layer since the late 1980s indicate that the subtropical gyre of the North Atlantic is at present not in a steady state.



**Figure 2** Interannual variability and trends of  $\Sigma\text{CO}_2$  and hydrography in the western North Atlantic near Bermuda (1970–2001). **a**, Difference between surface-layer and STMW  $\Sigma\text{CO}_2$  (in units of  $\mu\text{mol kg}^{-1}$ ) from 1970 to 2001.  $\Sigma\text{CO}_2$  data were sampled at BATS from October 1988 to September 2001 ('plus' symbols). BATS  $\Sigma\text{CO}_2$  data only were adjusted to account for the cyclo-stationary seasonal cycle. Also shown are data from 17 stations near Bermuda collected over the 1972–86 period.  $\Sigma\text{CO}_2$  data from 4 stations were collected in 1972–73 as part of the Geochemical Sections (GEOSECS) program (open circles).  $\Sigma\text{CO}_2$  data from 4 stations were collected in 1981 (open diamonds) as part of the Transient Tracer in the Ocean (TTO) program by T. Takahashi (Lamont Doherty Earth Observatory).  $\Sigma\text{CO}_2$  data from 2 stations were collected in 1984–85 at Hydrostation S by C. D. Keeling (Scripps Institution of Oceanography) (personal communication; triangle).  $\Sigma\text{CO}_2$  data from 7 stations were collected in 1985–86 (squares) at Hydrostation S by P. G. Brewer (Woods Hole Oceanographic institution)<sup>30</sup>. Although  $\Sigma\text{CO}_2$  was determined by different methods (potentiometry and manometry), these data sets are comparable to BATS data because we only compare surface and STMW values. The GEOSECS and TTO data sets are available at <http://www.cdiac.ornl.gov>. **b**, Interannual variability and trends of mixed-layer depth (bold line) and depth of the 18 °C isotherm (thin line) at BATS from October 1988 to September 2001 and at Hydrostation S from 1970 to 1988. Mixed-layer depth was calculated from CTD profiles and a 0.5  $\sigma_\theta$  criterion. STMW was not formed near Bermuda since 1987, during the BATS sampling period. Filled circles denote each year when STMW formed extensively across the subtropical gyre and as far south as Bermuda (32 °N). **c**, Interannual variability and trends of the temperature gradient in STMW ( $\delta T/\delta z_{\text{STMW}}$ ) expressed in °C per 100 m, using the methodology of ref. 7 and winter NAO conditions. Climate indices for NAO were compiled by the Climate and Global Dynamics (CGD) division at the National Centre for Atmospheric Research (NCAR; <http://www.cgd.ucar.edu/cas/climind/>). Wintertime (December–March) NAO indices were plotted as a solid line and based on sea-level pressure differences between Lisbon, Portugal and Stykkisholmur, Iceland<sup>9</sup>.  $\delta T/\delta z_{\text{STMW}}$  values (plus signs) at BATS were relatively high at  $\sim 0.2$ – $0.8$  °C per 100 m for the 1988–2001 period, indicating that STMW was not ventilated or formed near Bermuda during the winter.  $\delta T/\delta z_{\text{STMW}}$  values below 0.2 °C per 100 m are indicative of recent STMW renewal<sup>7</sup>. Dotted line is zero reference line for NAO index.

Table 1 Long-term trends for $\Sigma\text{CO}_2$ and other parameters at BATS			
Parameter	Slope and standard deviation ( $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ )	Number of observations	$r^2$
<b>Surface layer (observed trends)</b>			
$\Sigma\text{CO}_2$	$+1.32 \pm 0.18$	158	0.75
$n\Sigma\text{CO}_2$	$+1.25 \pm 0.14$	158	0.73
DO	$-0.42 \pm 0.08$	155	0.85
Temperature	$+0.009 \pm 0.016$	158	0.94
Salinity	$+0.001 \pm 0.003$	158	0.30
<b>Surface layer (inferred trends)</b>			
$dC_{\text{ani}}/dt$	+0.9	NA	NA
$dC_{\text{gasey}}/dt$	$+0.43 \pm 0.43$	158	0.49
$dC_{\text{bio}}/dt$	$-0.08 \pm 0.09$	158	0.22
<b>STMW (observed trends)</b>			
$\Sigma\text{CO}_2$	$+2.55 \pm 0.25$	96	0.56
$n\Sigma\text{CO}_2$	$+2.64 \pm 0.26$	96	0.55
$\Sigma\text{CO}_2/n\Sigma\text{CO}_2$ (26.4 $\sigma_\theta$ )	$+2.22 \pm 0.07$	94	0.65
DO	$-0.72 \pm 0.21$	91	0.17
Nitrate	$+0.07 \pm 0.02$	91	0.14
Phosphate	$+0.004 \pm 0.001$	88	0.15
Temperature	$-0.016 \pm 0.004$	95	0.23
Salinity	$-0.002 \pm 0.001$	96	0.16
<b>STMW (inferred trends)</b>			
$dC_{\text{ani}}/dt$	+0.9	NA	NA
$dC_{\text{gasey}}/dt$	$+1.07 \pm 0.25$	88	0.20
$dC_{\text{bio}}/dt$	$+0.55 \pm 0.17$	88	0.25

Long-term trends for  $\Sigma\text{CO}_2$ ,  $n\Sigma\text{CO}_2$  (that is,  $\Sigma\text{CO}_2$  normalized to a salinity of 36.6), dissolved oxygen (DO), nitrate, phosphate, temperature and salinity are computed for surface-layer and subtropical mode water (STMW) at the BATS site from October 1988 to September 2001. Regression statistics (slope, standard deviation, and  $r^2$ ) were determined using a least-squares fitting routine using a singular value decomposition method (see Methods). Statistical trends were also determined for the biological ( $C_{\text{bio}}$ ) and gas exchange ( $C_{\text{gasey}}$ ) contributions to the observed  $\Sigma\text{CO}_2$  trends (see Methods for details). The trend for the anthropogenic component ( $C_{\text{ani}}$ ) was estimated from the atmospheric  $\text{CO}_2$  trend assuming full equilibration between the atmospheric and oceanic perturbation. STMW is defined here by the 17.8–18.4 °C criterion and typically located at depths from 250 to 400 m. NA, not applicable.

Long-term changes of STMW  $\Sigma\text{CO}_2$  can only result from the uptake of anthropogenic  $\text{CO}_2$  from the atmosphere, from changes in the uptake of non-anthropogenic  $\text{CO}_2$  from the atmosphere through air–sea gas exchange at the site of STMW formation, or from variations in the remineralization of organic matter along the circulation pathway of the STMW. We evaluate the contributions of these processes to the  $\Sigma\text{CO}_2$  changes by using the long-term changes of inorganic nutrients as indicators of biological changes, by computing the anthropogenic  $\text{CO}_2$  contribution from thermodynamic considerations, and by estimating the gas-exchange component by difference. We thus consider the following components:

$$dC/dt = dC_{\text{ant}}/dt + dC_{\text{bio}}/dt + dC_{\text{gase}}/dt \quad (1)$$

where  $dC_{\text{ant}}/dt$  is the temporal change in ocean  $\Sigma\text{CO}_2$  as a result of the uptake of anthropogenic  $\text{CO}_2$  from the atmosphere,  $dC_{\text{bio}}/dt$  is the temporal change driven by biological processes such as primary production, remineralization and  $\text{CaCO}_3$  formation and dissolution<sup>19</sup>, and  $dC_{\text{gase}}/dt$  is the temporal change driven by variability in air–sea  $\text{CO}_2$  gas exchange as a result of changes in the seawater  $p_{\text{CO}_2}$  (partial pressure of  $\text{CO}_2$ ) conditions or wind speeds at the site of STMW formation (see Methods for details).

We estimate the rate of change of the anthropogenic component,  $dC_{\text{ant}}/dt$ , from the atmospheric  $\text{CO}_2$  change and the surface ocean buffer factor, assuming that near-surface waters in the subtropical gyres have residence times long enough to equilibrate entirely with the anthropogenic perturbation in atmospheric  $\text{CO}_2$ . This assumption is corroborated by long-term observations from various sites as well as many ocean modelling studies<sup>19</sup>. We obtain an equilibrium rate of  $\Sigma\text{CO}_2$  increase due to anthropogenic  $\text{CO}_2$  of  $+0.9 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (Fig. 1c), close to the observed rate of increase in surface ocean  $n\Sigma\text{CO}_2$  ( $+1.25 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ) at BATS. In the surface layer, with the exception of dissolved oxygen (DO), no significant changes in temperature, salinity, or inorganic nutrients were observed from 1988 to 2001 (Table 1). This suggests for the surface layer that long-term changes in the gas-exchange and biological components are small, and that the long-term change in  $\Sigma\text{CO}_2$  is primarily driven by the uptake of anthropogenic  $\text{CO}_2$  from atmosphere.

For STMW, the components that drive the temporal changes in  $\Sigma\text{CO}_2$  are summarized in Table 1 (see Methods and Supplementary Information). This analysis indicates that the rate of  $n\Sigma\text{CO}_2$  increase, in excess of equilibration with the anthropogenic perturbation of atmospheric  $\text{CO}_2$ , is at least  $1.6 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (that is,  $dC_{\text{bio}}/dt + dC_{\text{gase}}/dt = dC/dt - dC_{\text{ant}}/dt$ ). As the uptake of anthropogenic  $\text{CO}_2$  can only occur at the rate of equilibration or less, this is a lower-bound estimate for the change from gas exchange and biology. Closer inspection reveals that this anomalous increase is primarily due to an increase in the gas exchange component ( $dC_{\text{gase}}/dt = 1.07 \pm 0.25 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ) rather than a change in the biological component ( $dC_{\text{bio}}/dt = 0.55 \pm 0.17 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ). The long-term increase in  $C_{\text{bio}}$  in STMW is caused by an increase in the inorganic nutrients, and is associated with a long-term decrease in DO. This decrease in DO occurs in a nearly biological stoichiometric ratio to the increase in the inorganic nutrients, corroborating our interpretation (based on nutrient data) that the long-term increase in  $C_{\text{bio}}$  is due to a slightly enhanced accumulation of remineralized carbon in the STMW, either as a result of increased export or increased residence time of STMW. As there were no significant long-term changes of primary and export production observed over the 1988–2001 period near Bermuda<sup>15,20</sup>, we view this increase in  $C_{\text{bio}}$  as an indicator of increased residence time of STMW.

The large changes of the gas exchange component,  $C_{\text{gase}}$  (that is, the content of non-anthropogenic atmospheric  $\text{CO}_2$ ) in the STMW layer must have resulted from recent changes in the uptake of  $\text{CO}_2$  through gas exchange at the site of STMW formation. Air–sea gas exchange is typically parameterized as a quadratic or cubic function of wind speed<sup>21</sup> and  $\Delta p_{\text{CO}_2}$  (the gradient between air and sea of the

partial pressure of  $\text{CO}_2$ ,  $p_{\text{CO}_2}$ ). At the site of STMW formation, air-to-sea  $\text{CO}_2$  fluxes typically range from 5 to  $10 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$  (refs 15, 22) during winter time. If we assume a typical mixed layer thickness of  $\sim 400 \text{ m}$  at the site of STMW formation<sup>4,7</sup>, variability in the air–sea  $\text{CO}_2$  flux has the potential to change the  $\Sigma\text{CO}_2$  content of STMW by  $\sim 1\text{--}2 \mu\text{mol kg}^{-1}$  each winter. These estimates are consistent with the observed changes in STMW  $\Sigma\text{CO}_2$  and  $C_{\text{gase}}$  from 1988 to 2001. There has been a slight increase in mean winter (January–March) daily wind speed ( $\sim 0.03 \pm 0.04 \text{ m s}^{-1} \text{ yr}^{-1}$ ;  $r^2 = 0.10$ ) since 1980 in the STMW formation region, potentially equivalent to an increase in STMW  $\Sigma\text{CO}_2$  of  $\sim 0.06 \pm 0.08 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ . There are insufficient data to evaluate whether seawater  $p_{\text{CO}_2}$  conditions<sup>22</sup> have changed over time at the site of STMW formation (see Fig. 2b legend), but given the large variability in physical conditions at these sites, such changes appear very likely.

The fate of the non-anthropogenic atmospheric  $\text{CO}_2$  in STMW (that is, either eventual release to the atmosphere or transport to the ocean interior) may be linked to interannual variability of STMW formation and changes in NAO state. Extensive STMW formation, as far south as Bermuda, occurred during numerous winters in the 1960s and 1970s, and lastly in 1985 and 1987 (Fig. 2b, c), typically coinciding with NAO negative phases<sup>4,7,10</sup>. However, since 1987, winter STMW formation has been limited, coinciding with a predominantly NAO positive phase<sup>4,7,10</sup>. Winter mixing near Bermuda has been generally weak ( $< 200 \text{ m}$  deep), and not deep enough to entrain  $\Sigma\text{CO}_2$  from the STMW layer into the mixed layer at BATS (Fig. 2b). Analyses of the vertical temperature gradients within STMW<sup>7</sup> (that is,  $\delta T/\delta z_{\text{STMW}}$ ) also indicate that the STMW has not formed near Bermuda and that the STMW layer at BATS has not been ventilated recently (Fig. 2c), in agreement with our finding of a small increase in the  $C_{\text{bio}}$  component in the absence of a change in biological export. During this period of relatively weak winter mixing, atmospheric  $\text{CO}_2$  is retained and trapped in the STMW layer. As STMW is transported to the western boundary current, water parcels cool and sink to deeper depths in ‘cooling spirals’<sup>23,24</sup>, and  $\text{CO}_2$  is thereby transferred to deeper depths, constituting a potential long-term sink of  $\text{CO}_2$  ( $> 10 \text{ yr}$ ).

In contrast, during periods of extensive deep winter mixing ( $> 300\text{--}350 \text{ m}$  deep, before 1988, and primarily associated with NAO negative phases<sup>4,7,10</sup>), mixing entrains water from the STMW layer and ‘liberates’ atmospheric  $\text{CO}_2$  from STMW. We estimate that at least two-thirds of the STMW  $\text{CO}_2$  accumulation would be redistributed to seasonal thermocline waters overlying the STMW layer (see Methods). If this model is correct, atmospheric  $\text{CO}_2$  absorbed during STMW formation is only stored for short periods in STMW, thereby constituting a short-term sink of  $\text{CO}_2$  ( $< 3 \text{ yr}$ ). The relatively short observation period makes it difficult to demonstrate the proposed links between STMW variability, NAO changes and fate of  $\text{CO}_2$  within STMW. This is further complicated by the time delay of about 3–4 yr (ref. 11) between the time of STMW formation and the arrival of this signal near Bermuda.

The increase in  $C_{\text{gase}}$  implies a significant and recent change in the role of mode waters as an oceanic sink for atmospheric  $\text{CO}_2$ . Given current estimates about the volume of the North Atlantic STMW ( $1,672 \times 10^3 \text{ km}^3$ ; ref. 10), rates of STMW formation (5 to  $23 \text{ Sv}$ ;  $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ) and residence times<sup>5,25–29</sup>, and the  $\text{CO}_2$  increase (that is,  $dC_{\text{gase}}/dt + dC_{\text{bio}}/dt = 1.6 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ ), we estimate that  $\sim 0.4\text{--}2.8 \text{ Pg C}$  (or  $0.02\text{--}0.24 \text{ Pg C yr}^{-1}$ ) has accumulated in the subtropical gyre of the North Atlantic over the past 13 yr (see Methods and Supplementary Information). This accumulation of atmospheric  $\text{CO}_2$  in STMW, in excess of the rate of equilibration of anthropogenic  $\text{CO}_2$ , represents an extra oceanic sink of  $\text{CO}_2$  that is 3–10% of the average global uptake rate of  $\text{CO}_2$  ( $\sim 2 \text{ Pg C yr}^{-1}$ )<sup>3</sup> for the 1988–2001 period. In earlier decades, such as the 1970s and 1980s, extensive STMW ventilation of STMW across the gyre should have regularly ‘liberated’ a considerable amount of  $\text{CO}_2$  trapped in the STMW layer, thereby reducing the oceanic uptake of

atmospheric CO<sub>2</sub> into STMW. The present transfer of CO<sub>2</sub> via STMW to the ocean interior, facilitated by enhanced uptake of CO<sub>2</sub> and weak winter mixing, should continue until extensive deep winter mixing and STMW ventilation returns to the subtropical gyre. Interannual variability in the uptake, storage and transfer of STMW CO<sub>2</sub> to the ocean interior provides another factor and feedback controlling the global ocean uptake of CO<sub>2</sub>. □

## Methods

### Attribution of $\Sigma\text{CO}_2$ changes

We use the concept of quasi-conservative tracers<sup>19</sup> to separate the contribution of gas exchange, anthropogenic CO<sub>2</sub> and biological processes to the observed change in  $\Sigma\text{CO}_2$  over time ( $dC/dt$ ). We estimate the biological contribution to  $dC/dt$  from the temporal changes in the phosphate concentration ( $\text{PO}_4^{3-}$ ), nitrate concentration ( $\text{NO}_3^-$ ) and the changes in total alkalinity (TA), assuming constant stoichiometric ratios between carbon and phosphate during photosynthesis and respiration ( $r_{\text{C:P}} = 117:1$ )<sup>19</sup>. This gives  $dC_{\text{bio}}/dt = r_{\text{C:P}} d\text{PO}_4^{3-}/dt - 1/2(d\text{TA}/dt + d\text{NO}_3^-/dt)$ , where all concentrations are salinity normalized and given in  $\mu\text{mol kg}^{-1}$ . We estimate the anthropogenic change  $dC_{\text{ant}}/dt$  by assuming that surface waters in the subtropical gyre of the North Atlantic have followed the atmospheric perturbation and therefore have taken up anthropogenic CO<sub>2</sub> in equilibrium with anthropogenic CO<sub>2</sub> in the atmosphere. We compute  $dC_{\text{ant}}/dt$  using theoretical considerations of the oceanic carbonate system and the  $1.31 \mu\text{atm yr}^{-1}$  increase in atmospheric CO<sub>2</sub> observed at the island of Bermuda between 1988 and 2001 (data collected by NOAA Climate Monitoring and Diagnostics Laboratory at the Bermuda west station, and available at <http://www.cmdl.noaa.gov>). This yields a rate of increase of about  $0.9 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ . Finally, we estimate the change in  $\Sigma\text{CO}_2$  as a result of changes in gas exchange from the difference of the observed increase and the biological and anthropogenic changes, that is,  $dC_{\text{gasex}}/dt = dC/dt - dC_{\text{ant}}/dt - dC_{\text{bio}}/dt$ . As this last term is computed by difference, it contains all the accumulated errors made in the computation of  $dC_{\text{bio}}/dt$  and  $dC_{\text{ant}}/dt$ . However, as it turns out, the  $dC_{\text{bio}}/dt$  term is relatively small, and the uncertainty in the estimated equilibrium anthropogenic CO<sub>2</sub> change is small. Furthermore, the true anthropogenic CO<sub>2</sub> change can only be equal or smaller than the estimated equilibrium change, and therefore our estimated  $dC_{\text{gasex}}/dt$  term has to be regarded as a lower-bound estimate. If we allow for 20% uncertainty in both of our  $dC_{\text{bio}}/dt$  and  $dC_{\text{ant}}/dt$  estimates, our gas exchange term will be uncertain by about 20% as well.

### Estimate of long-term trends

We compute the long-term trends of the data by fitting the data to a function that includes a constant, a linear trend and harmonic terms with periods of 12, 6 and 4 months. The 8 unknown parameters of this fit are determined by minimizing the misfit between this function and the data in a least squares sense using singular value decomposition. In Table 1, only the parameter of the linear trend is given. The uncertainty of the parameters has been estimated from the square root of the variance of the fit multiplied with the square root of  $\chi^2/(N - 2)$ , where  $\chi^2$  is the minimized misfit and  $N$  is the number of data points.

### Estimate of STMW redistribution during winter deep mixing

Some portion of CO<sub>2</sub> within the STMW layer will be entrained into the seasonal thermocline during winters of deep mixing (>250–300 m). STMW typically has a thickness of 100–150 m, and is located at a depth of 250–400 m throughout the subtropical gyre, whereas the lower depth limit of the seasonal thermocline is typically 200–250 m. For example, if a 100-m-thick layer of STMW is entrained into a 300-m mixed layer during winter mixing, only one-third of the original STMW CO<sub>2</sub> will be retained within the STMW layer upon subsequent seasonal stratification (that is, 200 m deep). This redistribution should decrease or dilute  $\Sigma\text{CO}_2$  contents in the STMW layer and increase  $\Sigma\text{CO}_2$  contents in the seasonal thermocline.

### Estimate of oceanic sink of CO<sub>2</sub> in STMW layer since 1988

We estimate the oceanic sink of CO<sub>2</sub> from empirical and model understanding of the physical structure and circulation of the STMW layer in the subtropical gyre, and a simple input–output steady-state budget. We assume that the volume of the STMW is constant, which implies that input (STMW formation rate) equals output (subduction of STMW to deeper layers of the ocean). We furthermore assume that the observed rate of increase at BATS is representative for the entire STMW layer in the North Atlantic. The total accumulation of carbon in STMW ( $\Delta C_{\text{Inv}}$ ), where 'Inv' is the inventory of carbon can then be estimated by multiplying the 13-yr  $\Sigma\text{CO}_2$  increase ( $\Delta\Sigma\text{CO}_2 = dC/dt'$ , where  $t'$  is 13 yr) with the volume of STMW ( $V_{\text{STMW}}$ ). As the volume of STMW is somewhat uncertain, we can alternatively determine it from estimated STMW formation rates ( $\phi_{\text{STMW}}$ ) and residence times ( $\tau$ ). In summary, this gives:  $\Delta\text{Inv} = \Delta\Sigma\text{CO}_2 V_{\text{STMW}} = \Delta\Sigma\text{CO}_2 \tau \phi_{\text{STMW}}$ .

We estimate the volume of STMW between the permanent and seasonal thermocline in the North Atlantic using volume data computed for  $0.1 \sigma_\theta$  density layers by G. Daniels and D. Olson (Univ. Miami), with density derived from the temperature and salinity climatology of the World Ocean Atlas ([http://www.nodc.noaa.gov/OC5/data\\_woa.html](http://www.nodc.noaa.gov/OC5/data_woa.html)). This yields volumes of STMW in the North Atlantic of  $1.66 \times 10^{15} \text{ m}^3$ ,  $1.79 \times 10^{15} \text{ m}^3$ , and  $2.54 \times 10^{15} \text{ m}^3$  for the 26.4–26.6, 26.4–26.7 and 26.4–26.8  $\sigma_\theta$  layers, respectively. The 26.4–26.6  $\sigma_\theta$  density criterion compares well with previous estimates of the volume of STMW of  $1.67 \times 10^{15} \text{ m}^3$  (ref. 10). Lower (0.54 Pg C) and upper (2.23 Pg C) bound estimates of the CO<sub>2</sub> accumulation in STMW are determined on the basis of this range of volume estimates. For example, given the three different volumes of the STMW layer and a rate of  $n\Sigma\text{CO}_2$

increase of  $1.6 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (that is,  $dC_{\text{gasex}}/dt + dC_{\text{bio}}/dt$ ), we estimate the accumulation of CO<sub>2</sub> of 0.54, 0.58 and 0.90 Pg C, respectively, over the 1988–2001 period. A rate of  $n\Sigma\text{CO}_2$  increase of  $2.6 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (that is,  $dC_{\text{ant}}/dt + dC_{\text{gasex}}/dt + dC_{\text{bio}}/dt$ ) yields an accumulation of CO<sub>2</sub> of 0.88, 0.94 and 1.34 Pg C, respectively over the 1988–2001 period. In this scheme, we assume a mean residence time ( $\tau$ ) of 10 yr for water in the STMW layer. After STMW formation, the average time for a parcel of STMW to be transported from the site of formation to the western boundary current along the path of gyre recirculation has been reported as ranging from 6 to 14 yr (refs 11, 28, 29). <sup>3</sup>H/<sup>3</sup>He tracer data indicate that the typical age of water in STMW observed near Bermuda is 3–4 yr old<sup>11</sup>, with the age of STMW increasing along the mean geostrophic circulation pathway from the site of STMW formation to the western boundary current<sup>24,25</sup>. If  $\tau$  is shorter (that is, 6 yr), this would yield an accumulation of CO<sub>2</sub> of 1.47, 1.57 and 2.23 Pg C, respectively over the 1988–2001 period.

In the second approach, we use current knowledge about the annual rate of STMW formation and residence time of water in the STMW layer to estimate the total volume of the STMW layer. The annual supply of new STMW ( $\phi_{\text{STMW}}$ ) from the site of STMW formation has been estimated through empirical and model studies to range from 5 to 23 Sv (Sv =  $10^6 \text{ m}^3 \text{ s}^{-1}$ )<sup>5,25–27</sup>. As above, we assume a mean residence time ( $\tau$ ) of 10 yr for water in the STMW layer. Lower (0.32 Pg C) and upper (2.8 Pg C) bound estimates of the CO<sub>2</sub> accumulation in STMW are estimated using this method. For example, a rate of  $n\Sigma\text{CO}_2$  increase of  $1.6 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (that is,  $dC_{\text{gasex}}/dt + dC_{\text{bio}}/dt$ ) at three STMW formation rates (5, 14 and 23 Sv) yields an accumulation of CO<sub>2</sub> of 0.32, 0.90 and 1.47 Pg C, respectively over the 1988–2001 period. A rate of  $n\Sigma\text{CO}_2$  increase of  $2.6 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  (that is,  $dC_{\text{ant}}/dt + dC_{\text{gasex}}/dt + dC_{\text{bio}}/dt$ ) at the 3 STMW formation rates (5, 14 and 23 Sv) yields an accumulation of CO<sub>2</sub> of 0.61, 1.72 and 2.83 Pg C, respectively, over the 1988–2001 period.

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**Correspondence** and requests for materials should be addressed to N.B. (e-mail: [nick@bbsr.edu](mailto:nick@bbsr.edu)).

## The role of volatiles in magma chamber dynamics

Herbert E. Huppert & Andrew W. Woods

*Institute of Theoretical Geophysics, Department of Applied Mathematics and Theoretical Physics, Silver Street, Cambridge CB3 9EW, UK; and the BP Institute of Multiphase Flow, Madingley Rise, Madingley Road, Cambridge CB3 0EZ, UK*

Many andesitic volcanoes exhibit effusive eruption activity<sup>1</sup>, with magma volumes as large as  $10^7$ – $10^9$  m<sup>3</sup> erupted at rates of  $1$ – $10$  m<sup>3</sup> s<sup>-1</sup> over periods of years or decades. During such eruptions, many complex cycles in eruption rates have been observed, with periods ranging from hours to years<sup>2–7</sup>. Longer-term trends have also been observed, and are thought to be associated with the continuing recharge of magma from deep in the crust and with waning of overpressure in the magma reservoir. Here we present a model which incorporates effects due to compressibility of gas in magma. We show that the eruption duration and volume of erupted magma may increase by up to two orders of magnitude if the stored internal energy associated with dissolved volatiles can be released into the magma chamber. This mechanism would be favoured in shallow chambers or volatile-rich magmas and the cooling of magma by country rock may enhance this release of energy, leading to substantial increases in eruption rate and duration.

Consider a magma with bulk density  $\rho$  in a chamber of volume  $V$  undergoing a mass recharge rate  $Q_i$  and eruption rate  $Q_0$ , as sketched in Fig. 1. Conservation of mass indicates that:

$$\frac{d}{dt}(\rho V) = \rho \frac{dV}{dt} + V \frac{d\rho}{dt} = Q \quad (1)$$

where  $Q = Q_i - Q_0$ . The density of the magma, which consists of melt, crystals and gas, can be written, in general form, as  $\rho = \rho[p, T, x(T), N]$  where  $p$  is pressure,  $T$  temperature,  $x(T)$  the mass fraction of crystals in the magma and  $N$  the total mass fraction of volatiles. Depending on the pressure, a fraction of these volatiles are dissolved in the magma and the remainder exist in the gaseous phase. Differentiating this expression for the density and incorporating the result into equation (1), we obtain:

$$\frac{dV}{dt} + \frac{V \partial \rho}{\rho \partial p} \frac{dp}{dt} = \frac{Q}{\rho} - \frac{V \partial \rho}{\rho \partial T} \frac{dT}{dt} \quad (2)$$

where the second term on the right-hand side represents the rate of change of volume associated with the change in density with

temperature of the magma, which includes the effects of the change of crystal content with temperature, leading to an effective thermal expansion.

It is known<sup>8–10</sup> that the rate of change in volume of the chamber,  $dV/dt$ , is related to the associated rate of change in pressure,  $dp/dt$ , as a result of deformation of the surrounding rock by:

$$\frac{1}{\beta_r} \frac{dp}{dt} = \frac{1}{V} \frac{dV}{dt} \quad (3)$$

where  $\beta_r$  is the effective bulk modulus of the surrounding wall rock. The exact value of  $\beta_r$  depends on the density of microfractures in the rock, but a value of  $10^{10}$  Pa is typical<sup>10,11</sup>. Incorporating equation (3) into equation (2), we obtain:

$$V \left[ \frac{1}{\beta_r} + \frac{1}{\rho} \frac{\partial \rho}{\partial p} \right] \frac{dp}{dt} = \frac{Q}{\rho} - \frac{V \partial \rho}{\rho \partial T} \frac{dT}{dt} \quad (4)$$

Thus, as expressed by equation (3), the effective bulk modulus of the compressible magma,  $\beta$ , is given by:

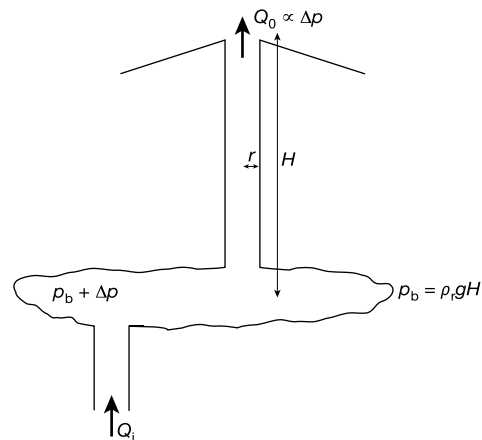
$$\frac{1}{\beta} = \frac{1}{\beta_r} + \frac{1}{\rho} \frac{\partial \rho}{\partial p} \quad (5)$$

We show here that for typical volatile-rich magmas, the second term on the right-hand side of equation (5) is much larger than the first term, which indicates that the compressibility of the saturated magma plus exsolved gas,  $C$ , defined as the inverse of the effective bulk modulus  $\beta$ , greatly exceeds that of the wall rock.

An explicit relationship for  $\rho$  in terms of the gas density  $\rho_g$ , the crystal density  $\rho_c$  and the melt density  $\rho_m$  is:

$$\rho = \left[ \frac{n}{\rho_g} + (1-n) \left( \frac{x}{\rho_c} + \frac{1-x}{\rho_m} \right) \right]^{-1} \quad (6)$$

where, to a good approximation, the gas density follows the ideal gas law<sup>12</sup>,  $\rho_g = p/RT$ , where  $R$  is the universal gas constant. We assume the exsolution of gas occurs at thermodynamic and chemical equilibrium, which is valid for the slow processes considered here<sup>13,14</sup>. Thus, in our model, the exsolved volatile content,  $n$ , follows from Henry's law<sup>12,13,15</sup>. This law, for water, which is frequently the dominant volatile species present, is  $n = N - sp^{1/2}(1-x) \geq 0$ , on the assumption that the magma is saturated, where  $s = 4 \times 10^{-6}$  Pa<sup>-1/2</sup> for water vapour. This will occur at sufficiently low pressures and sufficiently high total volatile or crystal contents. Alternatively, if  $sp^{1/2}(1-x) \geq N$ , the magma is undersaturated and  $n \equiv 0$ . Analogous calculations can be made for



**Figure 1** Schematic of magma reservoir. In the reservoir there is an overpressure  $\Delta p$  to a background pressure field at depth  $H$  given by  $p_b = \rho_r g H$ , where  $\rho_r$  is the density of the rocks above the magma chamber and  $g$  is the acceleration due to gravity. During a slow effusive eruption, through a conduit of radius  $r$ , mass is input at rate  $Q_i$  and erupted at rate  $Q_0$ .