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## Parameterizing bubble-mediated air-sea gas exchange and its effect on ocean ventilation

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[1] Bubbles play an important role in the exchange of gases between the atmosphere and ocean, altering both the rate of exchange and the equilibrium gas saturation state. We develop a parameterization of bubble-mediated gas fluxes for use in Earth system models. The parameterization is derived from a mechanistic model of the oceanic boundary layer that simulates turbulent flows and the size spectrum of bubbles across a range of wind speeds and is compared against other published formulations. Bubble-induced surface supersaturation increases rapidly with wind speed and is inversely related to temperature at a given wind speed, making the effect of bubbles greatest in regions that ventilate the deep ocean. The bubble-induced supersaturation in high-latitude surface waters compensates a substantial fraction of the undersaturation caused by surface cooling. Using a global ocean transport model, we show that this parameterization reproduces observed saturation rate profiles of the noble gas Argon in the deep Atlantic and Pacific Oceans. The abyssal argon supersaturation caused by bubbles varies according to gas solubility, ranging from  $\sim 0.7\%$  for soluble gases like  $\text{CO}_2$  to  $\sim 1.7\%$  for less soluble gases such as  $\text{N}_2$ . Bubble-induced supersaturation may be significant for biologically active gases such as oxygen.

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### 1. Introduction

[2] Oceanic-dissolved gas concentrations are governed by biogeochemical processes, such as photosynthesis/respiration that produce/consume dissolved gases [e.g., *Sarmiento and Gruber*, 2006] and by physical processes including gas transfer at the ocean surface, heating/cooling, bubbles [*Keeling*, 1993], and mixing [e.g., *Ito and Deutsch*, 2006]. Oceanic distributions of different gases have been used to quantify different physical and biogeochemical processes in the ocean. A few examples are the diagnosis of diapycnal mixing rate using argon (Ar) saturation levels [*Ito and Deutsch*, 2006; *Ito et al.*, 2007], the quantification of respiration rate using dissolved oxygen ( $\text{O}_2$ ) concentrations [*Jenkins*, 1982], and the determination of coastal bottom

water and the deep ocean ventilation at high latitudes [e.g., *Baschek*, 2003; *Nicholson et al.*, 2010]. Among the physical processes, the effect of bubbles is least understood and is most poorly quantified. Bubbles are entrained into the ocean during the breaking of surface gravity waves. They move under the action of boundary layer turbulence, rise by buoyancy, exchange gases with surrounding water, and change size due to the change of both gas amount and ambient pressure. Small bubbles, with slow buoyant rising velocities, are trapped in the boundary layer and dissolve completely. Large bubbles, with rapid buoyant rising velocities, are able to rise despite the downward turbulent motions and eventually burst at the ocean surface. As bubbles are compressed by hydrostatic pressure and surface tension, gases inside can be squeezed into the ocean even when it is supersaturated with respect to the atmosphere, causing gases to diffuse from the ocean to the atmosphere through the air-sea interface. Consequently, there is a gas supersaturation state, at which the gas flux through all bubbles are into the ocean, and this gas flux balances the diffusive gas flux from the ocean to the atmosphere through ocean surface (see top panel of Figure 1).

[3] Recent studies have shown that near-surface bubbles play an important role in the ocean-atmosphere exchange of gases at moderate to high wind speeds when bubbles are abundant [e.g., *Hamme and Emerson*, 2002, 2006; *D'Asaro and McNeil*, 2007; *Stanley et al.*, 2009; *Vlahos and Monahan*, 2009; *Vagle et al.*, 2010]. Bubbles influence

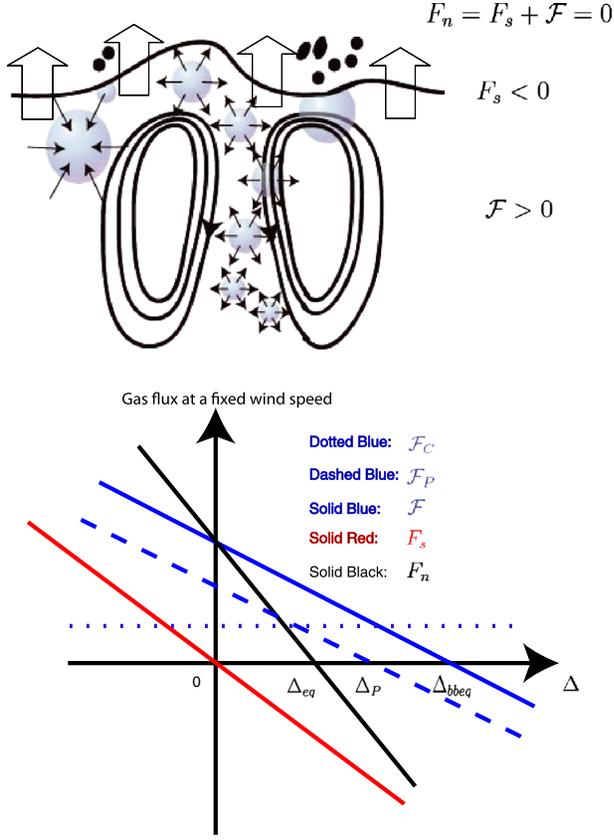
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**Figure 1.** (top) An illustration of the mechanism of bubble-induced equilibrium supersaturation. (bottom) A schematic diagram showing relations between different parameters defined in equations (2), (3), and (8).

air-sea gas transfer in two ways. First, bubbles provide an additional air-water interface for the transfer of gases, speeding the rate of equilibration. We refer to this as the “kinetic bubble effect.” Second, as bubbles are compressed by hydrostatic pressure and surface tension, gases inside can be squeezed into the surrounding seawater even when it is supersaturated with respect to the atmosphere, causing gases to diffuse from the ocean to the atmosphere through the air-sea interface. We refer to this as the “equilibrium bubble effect.” The combined effect of bubbles on air-sea gas transfer are the enhancement of air-sea gas transfer rate and the elevation of the saturation state at which the dissolved gases are in equilibrium with the atmosphere.

[4] In this study, we derive a parameterization using bubble fields at different wind speeds. The bubble fields are calculated using a multisize multigas bubble model embedded in a large-eddy simulation model for oceanic boundary layer including wave effects [Liang et al., 2011, 2012], which successfully simulates subsurface bubble evolution in turbulent oceanic boundary layers. This new parameterization, which is described in section 2, is compared with other published parameterizations [Woolf and Thorpe, 1991; McNeil and D’Asaro, 2007; Stanley et al., 2009; Vagle et al., 2010; Ito et al., 2011; Nicholson et al., 2011] in section 3. We then use a global transport model to evaluate the importance of bubble-induced equilibrium supersaturation level

for deep ocean ventilation. A summary and outlook is given in section 5.

## 2. A Physically Based Parameterization for Air-Sea Gas Transfer

### 2.1. Basic Formulae

[5] The conventional view of air-sea gas transfer, in the absence of bubbles, is that gases go in and out of the ocean through diffusion across the air-sea interface. The net gas flux  $F_n$  is the gas flux through the ocean surface  $F_s$  and is parameterized as

$$F_n = F_s = K_s C_{\text{sat}} \left( \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right), \quad (1)$$

where  $C_{\text{sat}} = S \chi_{\text{atm}} P_{\text{atm}}$  is the saturation that would be in equilibrium with one standard atmospheric pressure ( $P_{\text{atm}}$ ), with  $\chi_{\text{atm}}$  the gas fraction in the atmosphere, and with  $S$  the temperature-dependent solubility [Weiss, 1970; Hamme and Emerson, 2004].  $K_s$  is the gas transfer rate through ocean surface and is the only parameter in formula (1).  $P_{\text{slp}}$  is the local sea level pressure (SLP), and  $\sigma = \frac{C}{C_{\text{sat}}}$  is the saturation level with  $C$  the concentration of a dissolved gas. The amount of dissolved gas will also be presented by its saturation anomaly as [e.g., Emerson and Hedges, 2008]  $\Delta = \sigma - 100\%$ .

[6] This common formulation of diffusive surface gas exchange (equation (1)) can be modified to include both the equilibrium and kinetic effects of bubbles in a simple way [e.g., Woolf, 1997],

$$F_n = K_T C_{\text{sat}} \left[ (1 + \Delta_{\text{eq}}) \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right]. \quad (2)$$

Here  $K_T$  is the gas transfer rate through the ocean surface and bubbles and thus accounts for the kinetic effect of bubbles. The term  $\Delta_{\text{eq}}$  accounts for the equilibrium bubble effect and represents the bubble-induced supersaturation at which there is no net gas flux between the ocean and the atmosphere in steady state. When there are no bubbles in the water, i.e.,  $K_T = K_s$  and  $\Delta_{\text{eq}} = 0$ , equation (2) reduces to equation (1).

[7] In most ocean models that include gas exchange, the equilibrium bubble effect is neglected, i.e.,  $\Delta_{\text{eq}} = 0$ , while the kinetic effect is implicitly included in empirical estimates of  $K_T$  and its dependence on the 10 m wind speed  $u_{10}$ . The wind speed dependence of  $K_T$  has been investigated by laboratory measurements [e.g., Liss and Merlivat, 1986], deliberate tracer experiments in the open ocean [e.g., Wanninkhof et al., 1997; Nightingale et al., 2000; Ho et al., 2006], and atmospheric micrometeorological measurements above the open ocean [e.g., Fairall et al., 2000; Edson et al., 2011]. It is now generally accepted that  $K_T \propto u_{10}^2$  to  $u_{10}^3$  [e.g., Wanninkhof et al., 2009].

[8] The contribution of bubbles to gas exchange depends strongly on the bubble size, as large and small bubbles have qualitatively different fates. Large bubbles, with fast buoyant rising speeds, only partially dissolve before they eventually burst at the ocean surface. Small bubbles, with slow buoyant rising speeds, can be effectively trapped in the water, allowing the gas contents to completely dissolve [e.g., Keeling, 1993; Zhang, 2012]. In light of this distinction, the net gas

flux can then be formulated as [e.g., McNeil and D'Asaro, 2007; Stanley et al., 2009]

$$F_n = F_s + \mathcal{F}_P + \mathcal{F}_C$$

$$= K_s C_{\text{sat}} \left( \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right) + K_b C_{\text{sat}} \left( (1 + \Delta_P) \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right) + \mathcal{F}_C, \quad (3)$$

where the first term on the right represents gas exchange by ocean surface, the second term  $\mathcal{F}_P$  on the right represents gas through large bubbles that partially dissolve,  $K_b$  is the gas transfer rate through large bubbles,  $\Delta_P$  is the supersaturation due to partially dissolved bubbles, and the third term  $\mathcal{F}_C$  on the right represents gas flux through small bubbles that completely dissolve. Equation (3) is consistent with equation (2) if

$$K_T = K_b + K_s, \quad (4)$$

and

$$\Delta_{\text{eq}} = \frac{K_b C_{\text{sat}} \Delta_P \frac{P_{\text{slp}}}{P_{\text{atm}}} + \mathcal{F}_C}{K_T C_{\text{sat}} \frac{P_{\text{slp}}}{P_{\text{atm}}}}. \quad (5)$$

This expresses the equilibrium bubble effect in terms of all the fundamental parameters.

[9] A useful diagnostic expression of the impact of bubbles on the equilibrium gas supersaturation can be obtained from combining the two bubble terms,

$$\mathcal{F} = \mathcal{F}_P + \mathcal{F}_C$$

$$= K_b C_{\text{sat}} \left( (1 + \Delta_{\text{bbeq}}) \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right), \quad (6)$$

where

$$\Delta_{\text{bbeq}} = \Delta_P + \frac{\mathcal{F}_C}{K_b C_{\text{sat}} \frac{P_{\text{slp}}}{P_{\text{atm}}}}. \quad (7)$$

$\Delta_{\text{bbeq}}$  represents the saturation anomaly level when there is no net gas flux through all bubbles ( $\mathcal{F} = 0$ ). The combined gas flux through both the air-sea interface and bubbles can now be written using  $\Delta_{\text{bbeq}}$  as a single effective overpressure from both small and large bubbles,

$$F_n = F_s + \mathcal{F}$$

$$= K_s C_{\text{sat}} \left( \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right) + K_b C_{\text{sat}} \left( (1 + \Delta_{\text{bbeq}}) \frac{P_{\text{slp}}}{P_{\text{atm}}} - \sigma \right). \quad (8)$$

At this saturation anomaly level, gases added from small bubbles that completely dissolve ( $\mathcal{F}_C < 0$ ) is balanced by gas evasion into large bubbles ( $\mathcal{F}_P > 0$ ). Recall that when  $\Delta = \Delta_{\text{eq}}$ , there is no net gas flux through the ocean surface, i.e.,  $F_{\text{net}} = 0$ . At this saturation anomaly level, gases evade through the ocean surface ( $F_s > 0$ ), yet the net gas flux through all bubbles is dissolved ( $\mathcal{F} < 0$ ). Therefore,  $\Delta_{\text{bbeq}} > \Delta_{\text{eq}}$ . The relationship between different variables is illustrated in the bottom panel of Figure 1.

## 2.2. Determination of Parameters

[10] The total air-sea gas flux can be separated into a surface flux  $F_s$  and a bubble flux  $\mathcal{F}$ , as shown in equation (8). The surface flux is determined by a single parameter ( $K_s$ ), while three additional parameters ( $K_b$ ,  $\mathcal{F}_C$ , and  $\Delta_P$ ) are needed to compute bubble-mediated fluxes ( $\mathcal{F}$ ). The parameterization of surface gas flux is adopted from an existing model formula, allowing us to focus on a new model for the bubble-mediated component of exchange. These are discussed in the next two subsections, respectively.

### 2.2.1. Gas Transfer Through Ocean Surface

[11] In order to separate diffusive surface gas exchange from the bubble effects, we must use estimates of  $K_s$  that do not already include the influence of bubbles on the gas exchange rate. We use the surface gas flux parameterization for  $K_s$  in the NOAA-COAREG (National Oceanic and Atmospheric Administration Coupled Ocean-Atmosphere Response Experiment) gas transfer parameterization [Fairall et al., 2003, 2011; Hare et al., 2004]. The NOAA-COAREG algorithm is among the few gas flux parameterizations that explicitly separate  $K_s$  and  $K_b$ , with the former given by [e.g., Fairall et al., 2011]

$$K_s = \frac{u_*}{r_{\text{wt}} + \alpha r_a}, \quad (9)$$

where  $u_*$  is the friction velocity,  $r_{\text{wt}}$  is the waterside resistance to the transfer due to molecular turbulent processes,  $\alpha$  is the dimensionless solubility, and  $r_a$  is the atmosphere side resistance.  $r_{\text{wt}}$ ,  $\alpha$ , and  $r_a$  in equation (9) were estimated using formulas and parameters suggested by Fairall et al. [2011]. Surface gas transfer rate for other gases are estimated using the surface renewal theory by Fairall et al. [2011],

$$K_s^{\text{gas}} = K_s^{660} \left( \frac{Sc^{\text{gas}}}{660} \right)^{-1/2}, \quad (10)$$

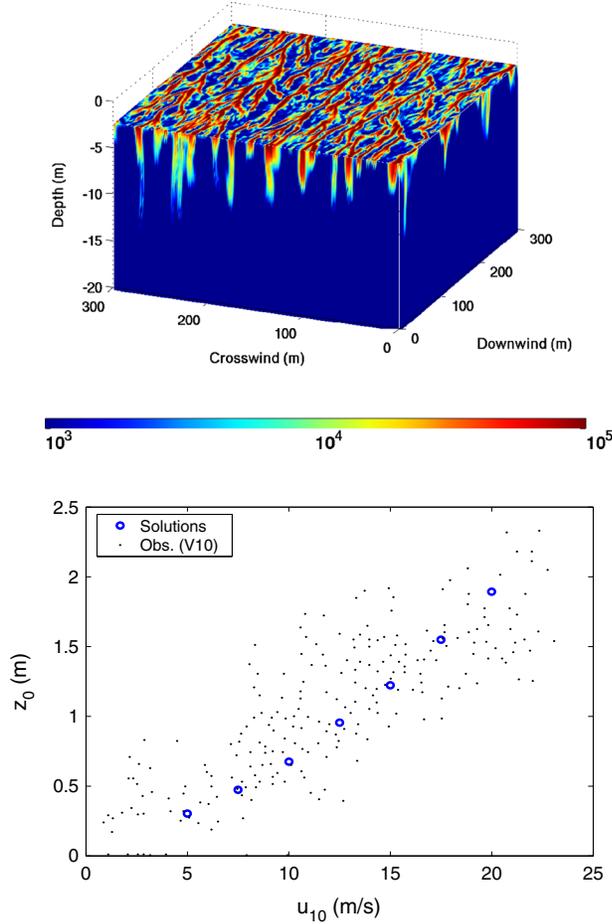
where  $Sc$  the Schmidt number and 660 is the value of  $Sc^{\text{CO}_2}$  at 20°C.

### 2.2.2. Gas Flux Through Bubbles

[12] Gas flux through bubbles can be estimated directly using subsurface bubble distribution [e.g., Woolf and Thorpe, 1991] or inversely using dissolved gas measurements [e.g., Stanley et al., 2009]. In this study, we take the former approach. The bubble distribution and associated gas fluxes are calculated using a large-eddy simulation (LES) model coupled to a bubble population model [Liang et al., 2011, 2012]; the important results of which are briefly described here.

[13] The coupled model simulates the simultaneous evolution of oceanic boundary layer turbulence and bubbles of 17 sizes (35  $\mu\text{m}$  to 1 cm) containing two gases ( $\text{O}_2$  and  $\text{N}_2$ ). In the model, waves were assumed in equilibrium with local winds, which vary in strength from 5–20 m/s. Bubbles are injected during wave breaking. Their spatial and size distributions are constrained by laboratory measurements [Deane and Stokes, 2002; Melville et al., 2002]. The ocean is covered by breaking waves of different lengths [e.g., Melville and Matusov, 2002]. The spatial distribution of bubbles under these breaking waves was calculated using a stochastic breaking wave model [Sullivan et al., 2004, 2007; McWilliams et al., 2012], which predicts a white cap coverage consistent with observations by Wu [1988]. The total amount of injected air conforms to observations that 50% of the breaking wave energy is consumed to deposit bubbles into the water [Lamarre and Melville, 1991]. The energy flux from breaking waves is parameterized following Terray et al. [1996] and is proportional to  $u_*^3$  for a given sea state.

[14] In a near-surface horizontal plane, bubbles are organized into downwind streaks by the surface convergent flows of Langmuir circulations (Figure 2 top panel). Below these streaks are bubble plumes penetrating to more than



**Figure 2.** (top) An instantaneous snapshot of simulated total bubble number density (number per  $\text{m}^{-3}$ ) at  $u_{10} = 17.5$  m/s. (bottom) Relationship between bubble e-folding depth  $z_0$  and wind speed  $u_{10}$ . (Black dots: observations by *Vagle et al.* [2010]; Blue circles: bubbly flow solutions assuming waves in equilibrium with local winds.)

10 m depth in the downward branches of Langmuir circulations. The near-surface streaks and intermittent bubble plumes have been observed in the ocean [*Farmer and Li, 1995; Vagle et al., 2010*]. Although the spatial distribution of bubbles seem intermittent, the vertical distribution of total bubble number can be well described by an exponentially decaying function with depth, i.e.,  $\int C_b dr \propto \exp\left(-\frac{z}{z_0}\right)$  with  $C_b(r, z)$  the horizontally and temporally averaged bubble number density distribution and  $z_0$  the bubble e-folding depth proportional to  $u_*$  for a given sea state. The oxygen fraction  $\chi_b^{O_2}$  decreases with depth because  $O_2$  dissolves faster than  $N_2$ . The numerical solutions have been validated against the few available observations [*Liang et al., 2011, 2012*]. The bubble penetration depth in the model compares well with observations from the North Pacific by *Vagle et al.* [2010] (Figure 2 bottom panel). A more detailed description of the model and solutions and their validation against available observations can be found in *Liang et al.* [2011, 2012].

[15] To estimate the necessary bubble parameters from the model solutions, we must first estimate the gas fluxes and

then use the results of section 2. Procedures for obtaining the three parameters are listed below:

[16] 1. *Compute gas flux from bubbles ( $\mathcal{F}$ )*. Gas flux between bubbles and water at saturation level  $\sigma$  can be calculated from LES solutions using  $C_b(r, z)$  and bubble gas fraction  $\chi_b(r, z)$  as

$$\mathcal{F}(\sigma) = \int_{-\infty}^0 \int_0^{\infty} \frac{dn}{dt}(r, z, \chi_b, \sigma) C_b(r, z) dr dz, \quad (11)$$

where  $\frac{dn}{dt}(r, z, \chi_b, \sigma)$  is the gas flux between a bubble of radius  $r$  at a depth  $z$  containing  $\chi_b$  fraction of the gas and water at saturation level  $\sigma$  and is calculated using parameters and formulas proposed by *Woolf and Thorpe* [1991] as  $\frac{dn}{dt}(r, z, \chi_b, \sigma) \propto (Sc)^{-2/3} S \left( \chi_b \frac{P_b}{P_{\text{atm}}} - \sigma \right)$ , with  $P_b = P_{\text{atm}} - \rho g z + \frac{2\gamma}{r}$  the pressure exerted on the bubble and  $\gamma$  the surface tension coefficient.

[17] 2. *Estimate gas transfer rate through large bubbles ( $K_b$ )*.  $\Delta_{\text{bbeq}}$  is sought by equating  $\mathcal{F}$  (formula (11)) to zero and noting that  $\Delta = \sigma - 100\%$ . According to equation (6), the gas transfer rate through bubbles  $K_b$  is then calculated by  $K_b = \frac{\mathcal{F}(100\%)}{\Delta_{\text{bbeq}} C_{\text{sat}}}$ .  $K_b$  for different gases can be scaled by  $Sc^{-2/3}$ , i.e.,  $K_b^{\text{gas}} = K_b^{660} \left( \frac{Sc^{\text{gas}}}{660} \right)^{-2/3}$ .

[18] 3. *Compute gas flux by completely dissolved bubbles ( $\mathcal{F}_C$ )*. The gas flux through completely dissolved bubbles is proportional only to gas fraction ( $\mathcal{F}_C^{\text{gas}} \propto \chi_{\text{atm}}^{\text{gas}}$ ), while the gas flux through partially dissolved bubbles has additional Schmidt number and solubility dependence ( $\mathcal{F}_P^{\text{gas}} \propto (Sc^{\text{gas}})^{-2/3} \chi_{\text{atm}}^{\text{gas}} S^{\text{gas}}$ ) [e.g., *Hamme and Emerson, 2002; Stanley et al., 2009*];  $\mathcal{F}_C$  can be estimated as  $\mathcal{F}_C = \frac{\mathcal{F}_P^{O_2} \chi_{\text{atm}}^{N_2} S^{N_2} (Sc^{N_2})^{-2/3} - \mathcal{F}_P^{N_2} \chi_{\text{atm}}^{O_2} S^{O_2} (Sc^{O_2})^{-2/3}}{\chi_{\text{atm}}^{O_2} \chi_{\text{atm}}^{N_2} S^{N_2} (Sc^{N_2})^{-2/3} - \chi_{\text{atm}}^{N_2} \chi_{\text{atm}}^{O_2} S^{O_2} (Sc^{O_2})^{-2/3}}$  with  $\mathcal{F}_C^{\text{gas}} = \mathcal{F}_C \chi_{\text{atm}}^{\text{gas}}$ .

[19] 4. *Estimate supersaturation by partially dissolved bubbles ( $\Delta_P$ )*. Having estimated the total gas flux and the flux from completely dissolved bubbles, the flux due to large bubbles can be computed by  $\mathcal{F}_P = \mathcal{F} - \mathcal{F}_C$ . According to equation (3),  $\Delta_P = \frac{\mathcal{F}_P(100\%)}{K_b^{\text{gas}} C_{\text{sat}}}$ .

[20] Having extracted the bubble fluxes and the critical parameters ( $K_b$ ,  $\mathcal{F}_C$ , and  $\Delta_P$ ) from the numerical solutions, we then relate them to meteorological conditions used to force the LES simulations. We plot each parameter against friction velocity  $u_*$  instead of the more commonly used  $u_{10}$ , because both injected bubble amount and bubble penetration depth depend directly on  $u_*$ . In this study,  $u_*$  is calculated as

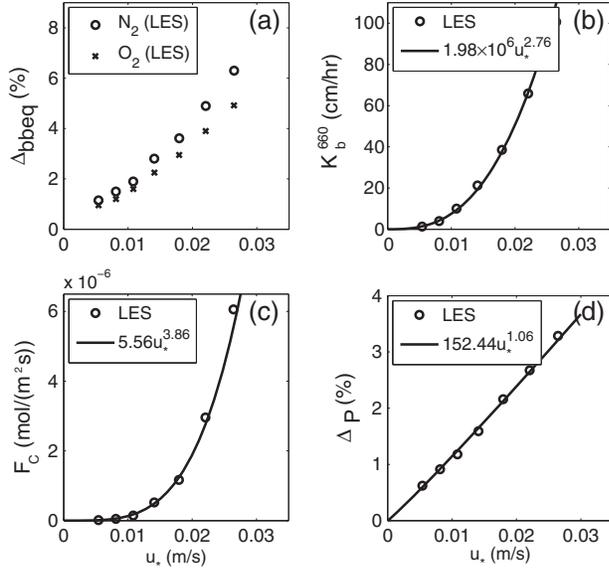
$$u_* = \sqrt{\rho_a C_d / \rho_w} u_{10}, \quad (12)$$

where  $\rho_a$  is the atmosphere density,  $\rho_w$  is the ocean density, and  $C_d$  is the drag coefficient parameterized following *Large and Pond* [1981] with its value saturated at 20 m/s as suggested by *Sullivan et al.* [2012],

$$C_d = \begin{cases} 0.0012 & \text{if } |u_{10}| \leq 11 \text{ m/s} \\ (0.49 + 0.0065|u_{10}|) \times 10^{-3} & \text{if } 11 \text{ m/s} < |u_{10}| < 20 \text{ m/s} \\ 0.0018 & \text{if } |u_{10}| \geq 20 \text{ m/s}. \end{cases} \quad (13)$$

Other formulas for  $u_*$  [e.g., *Fairall et al., 2011*] could also be substituted into the parameterization formulas below.

[21] We assume a power-law relationship between each bubble-related parameter and the friction velocity from the



**Figure 3.** (a)  $\Delta_{\text{bbeq}}$ : the saturation anomaly when the gas flux through all bubbles is zero, i.e.,  $\mathcal{F} = 0$ ), (b)  $K_b^{660}$  [cm/hr]: gas transfer rate through partially dissolved bubbles, (c)  $\mathcal{F}_C$  [mol/(m<sup>2</sup>s)]: gas transfer rate through partially dissolved bubbles, and (d)  $\Delta_P$ : supersaturation due to partially dissolved bubbles derived from the bubble solutions calculated by the coupled LES—bubble population model.  $K_T$ ,  $\Delta_{\text{bbeq}}$ ,  $\mathcal{F}_C$ , and  $\Delta_P$  are defined in equations (2), (3), (8), and the texts below the equations. The open circles are from LES solutions at  $u_{10} = [5 : 2.5 : 20]$  m/s.

model simulations. By a least squares regression, we get (see Figure 3)

$$K_b^{\text{gas}} = 1.98 \times 10^6 u_*^{2.76} \left( \frac{Sc^{\text{gas}}}{660} \right)^{-2/3} \text{ cm hr}^{-1}, \quad (14)$$

$$\mathcal{F}_C^{\text{gas}} = \chi_{\text{atm}}^{\text{gas}} 5.56 u_*^{3.86} \text{ mol s}^{-1} \text{ m}^{-2}, \quad (15)$$

and

$$\Delta_P = 152.44 u_*^{1.06} \%. \quad (16)$$

[22] Equations (3), (9), (14), (15), and (16) complete the parameterization for the total air-sea gas flux including the effect of gas bubbles. From them, the bubble-induced supersaturation ( $\Delta_{\text{eq}}$ ) can be obtained following equation (5).  $\Delta_{\text{eq}}$  increases with wind speeds (Figure 4). It is largest for least soluble gas ( $\text{N}_2$ ) and is smallest for most soluble gas ( $\text{CO}_2$ ). This is primarily because gas transfer through the ocean surface and partially dissolved bubbles is smaller for  $\text{N}_2$  than for  $\text{CO}_2$ ; the effect of completely dissolved bubbles is larger on  $\Delta_{\text{eq}}^{\text{N}_2}$  than on  $\Delta_{\text{eq}}^{\text{CO}_2}$ , i.e.,  $\frac{\mathcal{F}}{K_T C_{\text{sat}} \frac{p_{\text{slp}}}{p_{\text{atm}}}}$  in equation (5) is larger for  $\text{N}_2$  than for  $\text{CO}_2$  since  $\text{N}_2$  is less soluble than  $\text{CO}_2$ .

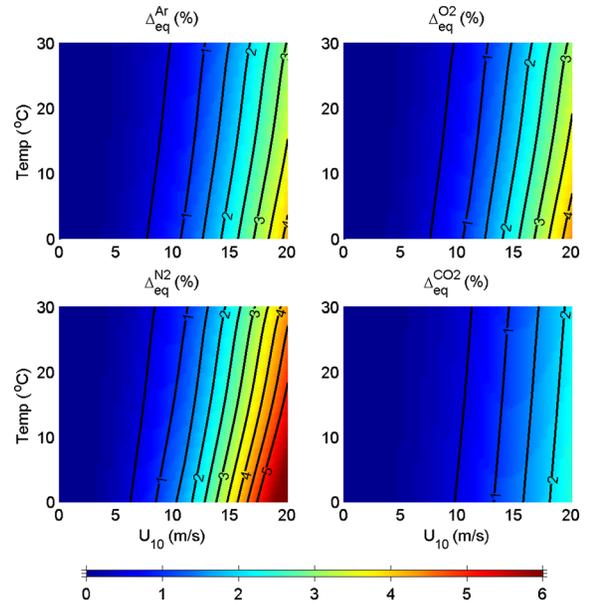
[23] A less obvious characteristics of  $\Delta_{\text{eq}}$  that has not been reported before is its temperature dependence.  $\Delta_{\text{eq}}$  and  $T$  are inversely correlated (Figure 4). When temperature increases,  $K_T C_{\text{sat}}$  increases because the enhancement of  $K_T$  by decreasing  $Sc$  dominates the decrease in  $C_{\text{sat}}$  by decreasing solubility. Therefore,  $\frac{\mathcal{F}_C}{K_T C_{\text{sat}} \frac{p_{\text{slp}}}{p_{\text{atm}}}}$  is smaller, and  $\Delta_{\text{eq}}$  is consequently smaller according to equation (5). Intuitively, turbulent diffusion and thus gas flux through both air-water

interface and partially dissolved bubbles are larger at higher temperature, yet the gas flux through completely dissolved bubbles does not change with temperature. Therefore, the supersaturation needed to create the outgassing flux that balances dissolution through completely dissolved bubbles is smaller at a higher temperature. The temperature dependence is larger for less soluble gases (e.g.,  $\text{N}_2$ ) because the relative contribution from completely dissolved bubbles is larger for these gases. The temperature dependence of  $\Delta_{\text{eq}}$  relies on the assumption that both bubble entrainment and penetration are independent of temperature. This assumption needs to be tested in the real ocean or laboratory. The uncertainties and caveats associated with this parameterization are detailed in the discussion section.

### 3. Comparisons With Other Parameterizations

[24] In this section, we compare the gas transfer parameterization derived in the previous section with five other existing air-sea gas transfer parameterizations including the effect of bubbles [Fairall *et al.*, 2011; Woolf and Thorpe, 1991; Stanley *et al.*, 2009; Vagle *et al.*, 2010; Ito *et al.*, 2011; Nicholson *et al.*, 2011] (Table 1). We included all available studies providing values for  $\Delta_{\text{eq}}$ . For the ease of comparison, all parameterizations are converted to a common form as equation (2). The parameter dependencies for each model are summarized in Table 1, and a brief summary of qualitative features is given below.

[25] Parameterizations CW and L12 (this study) both directly derived  $\Delta_{\text{eq}}$  from calculated bubble fields. Parameterization CW is in the form of equation (2).  $K_T$  is parameterized following NOAA-COARE algorithm, with a gas transfer rate through the ocean surface using equation (9) and a gas transfer rate through bubbles proportional to ocean surface whitecap coverage, i.e.,  $u_{10}^3$  [e.g., Asher *et al.*, 1996; Woolf, 1997; Monahan, 2001; Callaghan *et al.*, 2008].



**Figure 4.** Wind speed and temperature dependence of  $\Delta_{\text{eq}}$  (%) for four different gases (Ar,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$ ).

**Table 1.** Air-Sea Gas Transfer Parameterizations Including Bubble Effect<sup>a</sup>

Abbreviation	Source	Parameters
CW (COAREG+WT91)	<i>Fairall et al.</i> [2011]; <i>Wolf and Thorpe</i> [1991]	$K_s \propto u_*$ $K_b \propto u_{10}^3$ $\Delta_{eq} \propto u_{10}^2$
S09	<i>Stanley et al.</i> [2009]	$K_s \propto u_{10}^2$ $K_b \propto u_{10}^3$ $\mathcal{F}_C \propto u_{10}^3$ $\Delta_P \propto u_{10}$
V10	<i>Vagle et al.</i> [2010]	$K_T \propto u_{10}^{2.62}$ $\mathcal{F}_C \propto u_{10}^{3.33}$
I11	<i>Ito et al.</i> [2011]	$K_T \propto u_{10}^2$ $\mathcal{F}_C \propto u_{10}^3$
N11	<i>Nicholson et al.</i> [2011]	$K_T \propto u_{10}^2$ $K_b \Delta_P \propto u_{10}^3$ $\mathcal{F}_C \propto u_{10}^3$
L12	This study	$K_s \propto u_*$ $K_b \propto u_*^{2.76}$ $\Delta_P \propto u_*^{1.06}$ $\mathcal{F}_C \propto u_*^{3.86}$

<sup>a</sup>Definition of parameters are in section 2.1. Detailed descriptions of the parameterizations are in sections 2.2 and 3.

The parameters used in this study are those tuned to radiocarbon observations [*Jeffery et al.*, 2010]. The NOAA-COAREG algorithm, which does not include a parameterization for  $\Delta_{eq}$ , is combined with the  $\Delta_{eq}$  parameterization by *Wolf and Thorpe* [1991], who fitted a  $u_{10}^2$  dependence for  $\Delta_{eq}$  using bubble fields calculated by an individual bubble model.

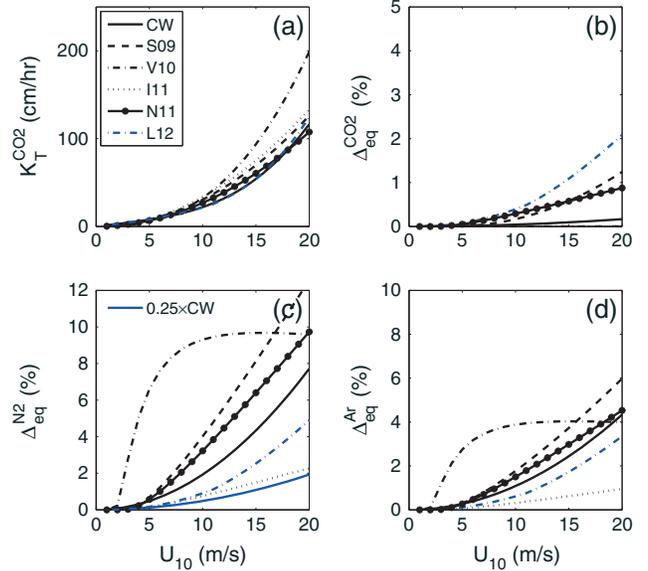
[26] The remaining parameterizations are based on dissolved gas observations. Parameterization S09 was proposed in the form of equation (3) [*Stanley et al.*, 2009]. It adopts the quadratic law by *Wanninkhof* [1992] for  $K_s$ .  $\Delta_P$  is proportional to  $u_{10}$ . The magnitudes of  $\mathcal{F}_C$  and  $K_b$  were tuned towards measured time series of upper ocean concentrations of five different inert gases (Ar, Kr, Xe, He, and Ne) at the Bermuda Atlantic Times-series Study (BATS) site. Parameterization V10 was proposed in the form of equation (3) but with  $\Delta_P = 0$  [*McNeil and D'Asaro*, 2007; *Vagle et al.*, 2010].  $K_T$  and  $\mathcal{F}_C$  were obtained by a least squares fit to time series of near-surface-dissolved  $N_2$  and  $O_2$  concentration near Ocean Station Papa at the North Pacific Ocean. It uses an inverse algorithm developed by *McNeil and D'Asaro* [2007] whose parameters were based on hurricane winds and is thus not considered here. Parameterization I11 was proposed in the same form as V10 [*Ito et al.*, 2011], with magnitudes of  $K_T$  and  $\mathcal{F}_C$  obtained by fitting a global mean surface Ne saturation level of 2%. Parameterization N11 was proposed in the form of equation (3) [*Nicholson et al.*, 2011], with parameter values determined by optimizing profiles of Ar, Ne,  $N_2/Ar$ , and  $Kr/Ar$  in a global transport model with observations at five different sites in the global ocean.

[27] The values for  $\Delta_{eq}$  in parameterizations S09, V10, I11, and N11 were inferred from observations of  $\Delta$  by removing the estimated contribution from heating/cooling, surface diffusive gas transfer, and mixing. An additional

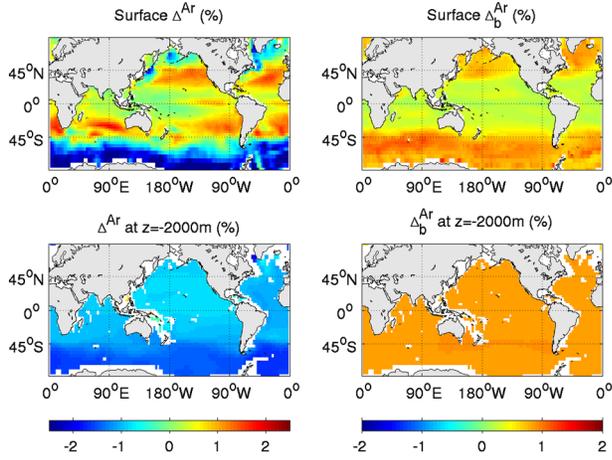
complication is that meteorological conditions other than wind speeds including wave age and surface heating/cooling modulate bubble distributions [*Wolf*, 2005; *Liang et al.*, 2012; *Vagle et al.*, 2012] and consequently  $\Delta_{eq}$ . Parameterizations CW and L12 both directly derive  $\Delta_{eq}$  from calculated bubble fields. In parameterization N11,  $N_2/Ar$  was used and this quantity is influenced by biogeochemical processes including denitrification [*DeVries et al.*, 2012] in addition to bubbles.

[28] All parameterizations predict similar trends and values for  $K_T^{660}$  (Figure 5a), and they are all within measured ranges [*Wanninkhof et al.*, 2009]. Other reported  $K_T^{660}$  [e.g., *Ho et al.*, 2006; *Wanninkhof et al.*, 2009; *Edson et al.*, 2011] span a wider range than shown in Figure 5a. They are not included in the comparison because they do not have a parameterization for  $\Delta_{eq}$ . In contrast, the values for  $\Delta_{eq}$  at a given temperature differ significantly among parameterizations.

[29] Values for  $\Delta_{eq}^{CO_2}$  from S09, N11, and L12 are substantially larger than other parameterizations (Figure 5b). This is because these three parameterizations explicitly include the contributions from bubbles that partially dissolve, i.e.,  $\Delta_P$ , while the other three do not. The contribution from partially dissolved bubbles may be overestimated in these three parameterizations however, since they have not considered the possibility that  $CO_2$  has equilibrated with the ambient water in intermediate-size bubbles while  $O_2$  and  $N_2$  have not (see section 5).  $\Delta_{eq}^{CO_2} > 1\%$  at  $u_{10} = 20$  m/s for S09 and L12.  $\Delta_{eq}^{CO_2}$  in L12 increases faster with wind speed than in S09 and N11. In S09 and N11, the wind speed dependence of bubble-mediated gas flux is assumed the same as for whitecap coverage, i.e., proportional to  $u_{10}^3$ . However, recent



**Figure 5.** Wind speed dependence of (a)  $K_T^{CO_2}$  (cm/hr), (b)  $\Delta_{eq}^{CO_2}$  (%), (c)  $\Delta_{eq}^{N_2}$  (%), and (d)  $\Delta_{eq}^{Ar}$  (%) at 20°C using different parameterizations.  $K_T$  and  $\Delta_{eq}$  are defined in equation (2) and the text below.  $\frac{1}{4}$  of  $\Delta_{eq}^{N_2}$  by *Wolf and Thorpe* [1991] is also plotted in Figure 5c because *Vagle et al.* [2010] found that model results agree better with their observations with the formula. Keys in the legend are explained in Table 1.



**Figure 6.** Maps of  $\Delta^{\text{Ar}}$  (%) (left panels) and  $\Delta_b^{\text{Ar}}$  (%) (right panels) at the surface and 2000 m depth.

studies [McNeil and D’Asaro, 2007; Chiba and Baschek, 2010; Liang et al., 2012] show that the wind speed dependence of bubble-mediated gas flux is between  $u_{10}^5$  and  $u_{10}^6$  because both bubble injection and bubble penetration is a function of  $u_{10}$ .

[30] Figure 5c displays  $\Delta_{\text{eq}}^{\text{N}_2}$  from different parameterizations. Besides the six parameterizations shown in Figures 5a and 5b, a line showing 0.25 of the  $\Delta_{\text{eq}}^{\text{N}_2}$  in CW is added, as Vagle et al. [2010] reported that  $0.25 \times \Delta_{\text{eq}}^{\text{N}_2}$  in CW better reproduces their observations than the original formula in CW.  $\Delta_{\text{eq}}^{\text{N}_2}$  is larger than  $\Delta_{\text{eq}}^{\text{CO}_2}$  for the reason explained in section 2. The values for  $\Delta_{\text{eq}}^{\text{N}_2}$  in different parameterizations also span a wide range. At  $u_{10} = 20$  m/s,  $\Delta_{\text{eq}}^{\text{N}_2}$  varies from about 2% (I11) to more than 12% (S09). Parameterization V10 predicts a distinctly different wind speed dependence for  $\Delta_{\text{eq}}^{\text{N}_2}$ , increasing sharply at low wind speed and leveling off at  $u_{10} > 8$  m/s. This is because V10 did not prescribe the functional form of the wind speed dependence, in contrast to other gas-based models. Although values for  $\Delta_{\text{eq}}^{\text{N}_2}$  from  $0.25 \times \text{CW}$ , I11, and L12 are close at  $u_{10} < 10$  m/s, their wind speed dependence is different among the three parameterizations.  $\Delta_{\text{eq}}^{\text{N}_2}$  from L12 shows the strongest wind speed dependence. Parameterizations for  $\Delta_{\text{eq}}^{\text{Ar}}$  show similar behavior as for  $\Delta_{\text{eq}}^{\text{N}_2}$ , except that values for  $\Delta_{\text{eq}}^{\text{Ar}}$  are smaller than for  $\Delta_{\text{eq}}^{\text{N}_2}$  (Figures 5d) because argon is slightly more soluble than nitrogen. The value for  $\Delta_{\text{eq}}^{\text{O}_2}$  is similar to the value for  $\Delta_{\text{eq}}^{\text{Ar}}$  and is not shown here. The ratio of  $\Delta_{\text{eq}}$  between relatively insoluble gases (Ar and  $\text{N}_2$ ) and soluble gas ( $\text{CO}_2$ ) is larger in parameterization S09 than in parameterization L12. In parameterization S09 [Stanley et al., 2009], more than 95% of the gas flux through bubbles comes from completely dissolved bubbles for relatively insoluble gases. In parameterization L12, the respective contributions from completely dissolved bubbles and from partially dissolved bubbles are comparable for relatively insoluble gases, as observed by Hamme and Emerson [2006].

[31] The temperature dependence reported in section 2 exists in all parameterizations listed in Table 1 except parameterization CW (not shown). Parameterization CW does not predict a temperature dependence for  $\Delta_{\text{eq}}$  because it specifies a wind speed only dependence for  $\Delta_{\text{eq}}$ .

#### 4. Importance in Ocean Ventilation

[32] In this section, we assess the importance of bubble-induced equilibrium supersaturation state ( $\Delta_{\text{eq}}$ ) in ocean ventilation using a global transport model. We illustrate the role of bubbles using the inert gas argon because it is subject only to physical processes, including heating/cooling, mixing, and bubble processes, but has similar chemical properties to  $\text{O}_2$ . Argon has been commonly used to separate the contribution of physical processes on the saturation state of biogeochemically important gases, such as  $\text{O}_2$  and  $\text{N}_2$ . For example,  $\text{O}_2$  to Ar ratio has been used to quantify production/respiration [e.g., Hamme et al., 2012], and  $\text{N}_2$  to Ar ratio has been used to quantify denitrification [e.g., Devola et al., 2006; DeVries et al., 2012]. The bubble effects are also presented for biologically active gases,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$ , based on simulations without biological sources and sinks.

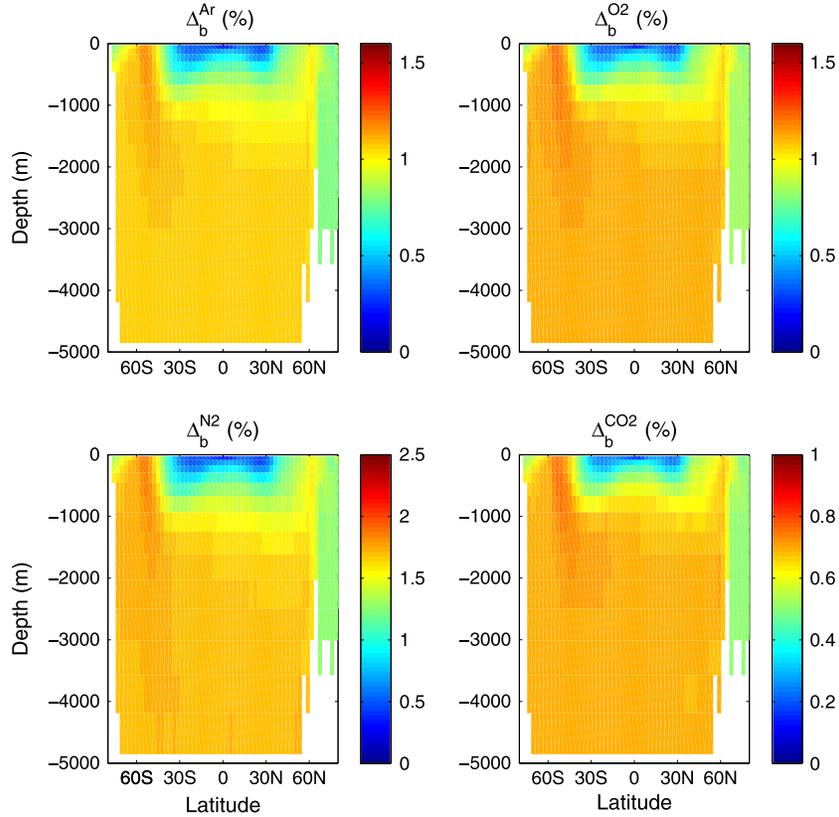
[33] The steady state concentrations of a tracer ( $\bar{c}$ ) in the global ocean are calculated using the transport matrix method [Khatiwala et al., 2005; Khatiwala, 2008]. This approach is much faster than a full general circulation model run and allows us to test different parameterizations in a short time. The model solves the equation

$$\bar{A}\bar{c} = \frac{\bar{F}}{\delta z_0}, \quad (17)$$

where  $\bar{A}$  is the transport matrix representing the advection and diffusion of a tracer with concentration  $\bar{c}$ ,  $\bar{F}$  is the air-sea gas flux of the tracer, and  $\delta z_0$  is the thickness of surface grid cell. In this study,  $\bar{A}$  was derived from a solution of the Massachusetts Institute of Technology general circulation model (MITgcm) [Marshall et al., 1997; Khatiwala et al., 2005] that was configured with a horizontal resolution of  $2.8^\circ$  and 15 surface-intensified levels with the first level at 25 m depth.

[34] Air-sea gas flux parameters were calculated using daily climatological ocean surface conditions. The calculated daily gas fluxes were then averaged over a year. Sea level pressure originated from the National Centers for Environmental Prediction reanalysis [Kanamitsu et al., 2002], and surface wind speeds were derived from QuikSCAT scatterometer wind (<http://podaac.jpl.nasa.gov/OceanWind/QuikSCAT>). The calculated gas flux was then multiplied by the ice-free fraction from Ocean Carbon-cycle Model Intercomparison Project Phase 2. Because the wind speed dependence of the air-sea gas flux is nonlinear, the use of wind speeds of lower temporal frequencies will yield smaller-averaged air-sea gas flux [Sarmiento and Gruber, 2006], i.e.,  $\left(\frac{1}{t_2-t_1} \int_{t_1}^{t_2} u_{10} dt\right)^n < \frac{1}{t_2-t_1} \int_{t_1}^{t_2} u_{10}^n dt$  when  $n > 1$ .

[35] We performed two sets of experiments. The first set of experiments are taken as control runs. In these experiments, parameterizations for both  $K_T$  and  $\Delta_{\text{eq}}$  described in the previous section are used. The second set of experiments are designed to represent existing climate simulations, in which only the parameterization for  $K_T$  is used and  $\Delta_{\text{eq}}$  is set to zero, i.e.,  $F_n$  is calculated by equation (2) with  $\Delta_{\text{eq}} = 0$ . This set of experiments mimics typical climate models by neglecting the equilibrium bubble effect and will be denoted as “No  $\Delta_{\text{eq}}$  run” in the rest of the paper. The difference between the two sets of experiments is the supersaturation



**Figure 7.** Zonally averaged vertical profiles of  $\Delta_b^{\text{Ar}}$  (%) for four different gases (Ar, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>).

state caused solely by bubble-induced supersaturation state  $\Delta_b$ , i.e.,

$$\Delta_b = [\Delta]_{\text{controlrun}} - [\Delta]_{\text{no}\Delta_{\text{eq}}\text{run}}. \quad (18)$$

The geographic distribution of  $\Delta^{\text{Ar}}$  in runs forced by L12 is shown in Figures 6 and 7. Gas fluxes calculated by other parameterizations yield similar patterns, although the values are different (not shown).

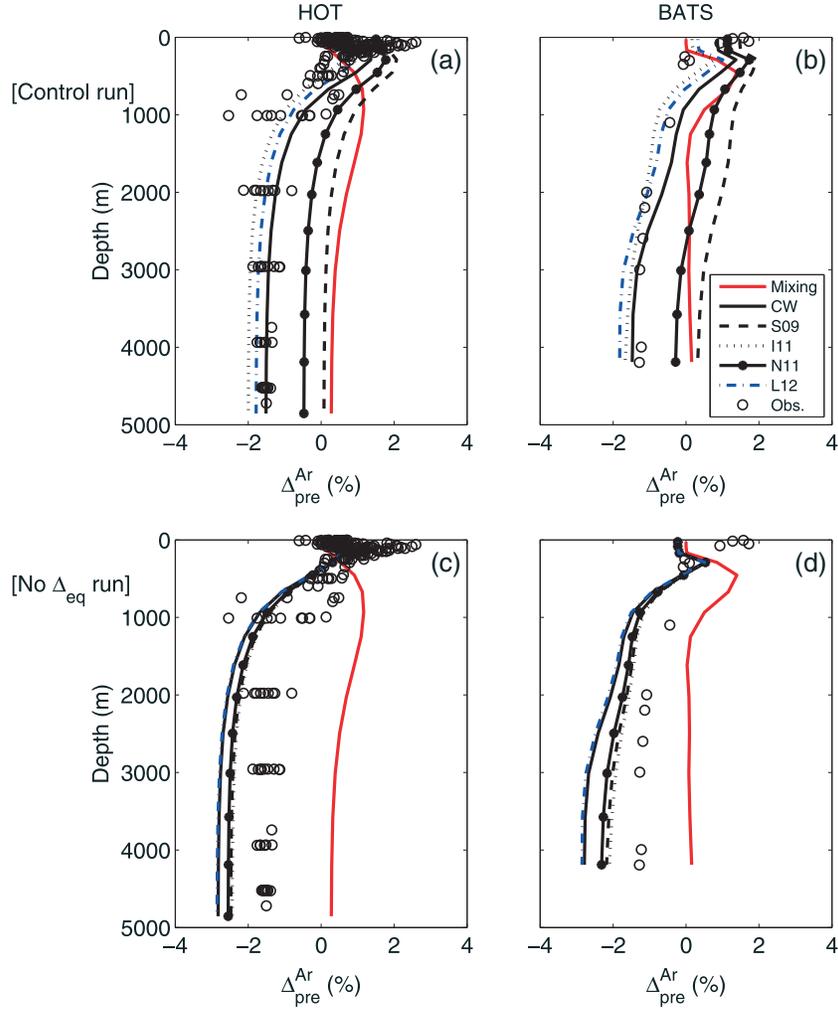
[36] Besides the two sets of experiments, an experiment with fast gas exchange is used to calculate the mixing induced supersaturation  $\Delta_{\text{mix}}$  [Ito *et al.*, 2011]. In this experiment, SLP is set everywhere with one standard atmospheric pressure and  $K_T$  is set to a large value. The surface ocean is therefore everywhere 100% saturated, and any interior supersaturation is consequently caused only by mixing.

[37] Surface-dissolved argon is more than 2% undersaturated at high latitudes (poleward of 60° in both hemispheres), indicating oceanic uptake of Ar. At the eastern side of the basin at low latitude and midlatitude and at the tropics, near-surface  $\Delta^{\text{Ar}}$  is positive and outgassing occurs. Ingassing at high latitudes and outgassing at low latitudes and midlatitudes are consistent with the oceanic cycle of other dissolved gases such as CO<sub>2</sub> [Toggweiler *et al.*, 2003]. The undersaturation at high latitudes and supersaturation at low latitudes is driven by cooling and warming, respectively, while air-sea gas fluxes reduce the latitudinal saturation contrast. Higher/lower gas transfer rate (larger/smaller  $K_T$ ) leads to smaller/larger latitudinal saturation contrast. In the abyss (2000 m depth), the ocean is more than 1% undersaturated.

The deep saturation anomaly is much more spatially uniform than near the surface.

[38] The bubble effect ( $\Delta_b^{\text{Ar}}$ ) is everywhere larger than zero at both the ocean surface and the ocean interior. At the ocean surface,  $\Delta_b^{\text{Ar}}$  is more than 1% supersaturated at the southern ocean where the cooling-driven undersaturation is also high. Both the high wind speed and low temperature in this region are favorable for the equilibrium bubble effect (large  $\Delta_{\text{eq}}^{\text{Ar}}$ ) and, therefore, drive larger  $\Delta_b^{\text{Ar}}$  than at the low-latitude and midlatitude surface ocean. Surface  $\Delta_b^{\text{Ar}}$  at high latitudes of the North Atlantic and the North Pacific are slightly smaller than at the Southern Ocean but is also higher than at the low latitudes and midlatitudes.  $\Delta_b^{\text{Ar}}$  in the ocean interior is much more spatially uniform than at the surface and is close to  $\Delta_b^{\text{Ar}}$  of Southern Ocean surface.

[39] The processes underlying deep ocean saturation levels can be understood by examining meridional cross sections of gas saturation states (Figure 7). South of 45°S, Antarctic Bottom Water and Antarctic Intermediate water transport positive  $\Delta_b^{\text{Ar}}$  north to the deep water of all three basins. In the Northern Hemisphere, North Atlantic Deep Water also transports positive  $\Delta_b^{\text{Ar}}$  into the deep ocean, while the North Pacific Intermediate Water subducts positive  $\Delta_b^{\text{Ar}}$  to between 1000 and 2000 m depth. The zonally averaged  $\Delta_b$  for three other gases (O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>) exhibit similar spatial patterns to Ar but with different magnitudes (Figure 7).  $\Delta_b^{\text{CO}_2}$  is possibly overestimated since the parameterization has not considered the possibility that CO<sub>2</sub> in partially dissolved bubbles equilibrate with ambient water. For a given wind speed,  $\Delta_{\text{eq}}$  is largest for N<sub>2</sub> and smallest for CO<sub>2</sub>; therefore,  $\Delta_b$  is largest for N<sub>2</sub> and smallest for CO<sub>2</sub>.



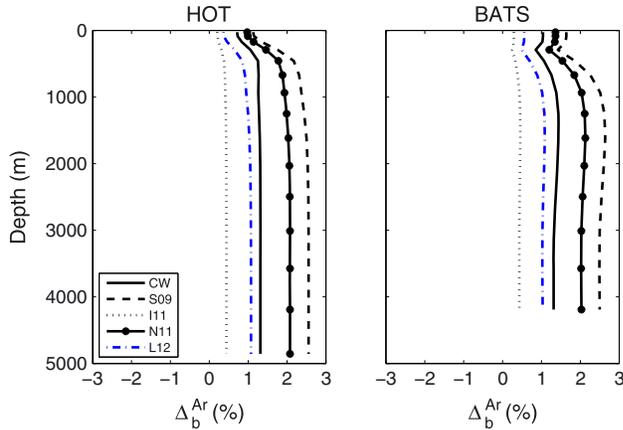
**Figure 8.** Profiles of  $\Delta_{\text{pre}}^{\text{Ar}}$  and  $\Delta_{\text{mix}}^{\text{Ar}}$  (%) at the Hawaiian Ocean Time-series (HOT) site (left panels) and at the Bermuda Atlantic Time-series Study (BATS) site (right panels). Top panels are results from the control runs, and bottom panels are results from the no  $\Delta_{\text{eq}}$  runs. The solution using parameterization V10 is not presented, as its prediction is strongly influenced by the large  $\Delta_{\text{eq}}$  at low wind speeds (see Figure 5). Observations were obtained by *Hamme and Emerson* [2002]. Keys in the legend are explained in Table 1.

[40] The importance of bubbles for the saturation state of the deep ocean can be evaluated by comparing predictions from gas exchange models to inert gas observations. Observed profiles of argon from the Hawaii Ocean Time-series (HOT) site in the Pacific Ocean and the Bermuda Atlantic Time-series Study (BATS) site in the Atlantic Ocean provide a measure of the vertical and basin-scale Ar concentration gradients.

[41] To compare model-simulated saturation states to observations, we first subtract the supersaturation that arises due to mixing of gases with nonlinear thermal solubilities across oceanic temperature gradients [*Ito and Deutsch, 2006*]. These mixing effects are exaggerated by spurious numerical diffusion in coarse circulation models. Following *Ito and Deutsch* [2006],  $\Delta^{\text{Ar}}$  can be separated into a preformed component  $\Delta_{\text{pre}}^{\text{Ar}}$  and a mixing component  $\Delta_{\text{mix}}^{\text{Ar}}$ , i.e.,  $\Delta^{\text{Ar}} = \Delta_{\text{pre}}^{\text{Ar}} + \Delta_{\text{mix}}^{\text{Ar}}$ .  $\Delta_{\text{pre}}^{\text{Ar}}$  is the combined consequence of surface gas exchange processes including bubble-induced supersaturation states ( $\Delta_{\text{eq}}$ ) and the heating/cooling during the transit of surface water into the deep ocean. It is

calculated by subtracting  $\Delta_{\text{mix}}$  estimated in the run with fast gas exchange from  $\Delta$  in the control run and the no  $\Delta_{\text{eq}}$  run.

[42] Argon concentrations at different depths reflect surface processes at different locations and physical process during their transit in the ocean. In the control runs,  $\Delta_{\text{pre}}^{\text{Ar}}$  decreases with water depth; however, the deep ocean  $\Delta_{\text{pre}}^{\text{Ar}}$  span a wide range among parameterizations (Figures 8a and 8b). Parameterizations S09 and N11 predict larger values than observations at both sites. Modeled abyssal  $\Delta_{\text{pre}}^{\text{Ar}}$  using the other three parameterizations (CW, I11, and L12) are close to observed values at both sites. Figures 8c and 8d compare modeled  $\Delta_{\text{pre}}^{\text{Ar}}$  profile from the no  $\Delta_{\text{eq}}$  runs with observations. Difference in the results in these runs arises from the difference in  $K_T$ . Faster/slower gas transfer (larger/smaller  $K_T$ ) offsets more/less cooling-driven undersaturation at high-latitude surface ocean and predicts smaller/larger undersaturation in the abyss. Calculated no  $\Delta_{\text{eq}}$  run profiles have similar shapes as in the control runs (Figures 8a and 8b). Results using different parameterizations differ much less than in the control runs, primarily



**Figure 9.** Profiles of  $\Delta_b^{\text{Ar}}$  (%) at the two sites. Keys in the legend are explained in Table 1.

because the values for  $K_T$  in all the parameterizations are similar. The similar results among the no  $\Delta_{\text{eq}}$  runs imply that the difference shown in modeled  $\Delta_{\text{Ar}}$  in the control runs mainly comes from the difference of  $\Delta_{\text{Ar}}^{\text{pre}}$  in different parameterization schemes. As mentioned in section 3, observed  $K_T$  has a larger variability than the parameterizations chosen here. All runs using parameterizations excluding the effect of bubble-induced equilibrium supersaturation underestimate observed  $\Delta^{\text{Ar}}$ .

[43] Figure 9 shows the profiles of  $\Delta_b^{\text{Ar}}$  at both sites. The values of  $\Delta_b^{\text{Ar}}$  are higher at depth than near surface, because  $\Delta_b^{\text{Ar}}$  at depth originates from surface  $\Delta_b^{\text{Ar}}$  at high latitudes where wind speeds are higher and temperatures are lower than at the surface of both sites.  $\Delta_b^{\text{Ar}}$  is the primary cause of the difference of  $\Delta_{\text{Ar}}^{\text{pre}}$  and consequently the difference of  $\Delta_b^{\text{Ar}}$  between different parameterizations. The abyssal  $\Delta_b^{\text{Ar}}$  is between 0.4% (I11) and 2.6% (S09) at the HOT site and between 0.4% and 2.5% at the BATS site.

[44] Model runs shown above are driven by annual mean transport matrix. The abyssal  $\Delta^{\text{Ar}}$  is controlled by surface  $\Delta^{\text{Ar}}$  at high latitudes where deep waters form. Deep waters preferentially form in winter [Marshall and Schott, 1999] when the oceanic temperature is lower, the wind speed is higher, and the sea ice coverage is higher than in other seasons. The different winter time conditions have different impact on high-latitude surface and abyssal saturation levels. Lower temperature drives larger undersaturation. Both the slower gas transfer under lower temperature (the effect of convection which possibly enhances gas transfer rate [e.g., Rutgersson et al., 2011] is neglected in all the parameterizations used in this study) and the smaller gas flux due to higher ice coverage further drive larger undersaturation. However, lower temperature implies larger bubble-induced surface equilibrium supersaturation ( $\Delta_{\text{eq}}$ ) and reduces undersaturation. Higher wind speed also reduces undersaturation by driving faster gas transfer and larger bubble effect. The combined effect of all these conditions deserves further study in the future.

## 5. Discussion and Outlook

[45] Our results provide a first-order estimate of bubble-induced equilibrium saturation state and its effect in the

global ocean by relating gas flux through bubbles to wind speed and using an ocean circulation model to propagate saturation level set by these fluxes into the ocean interior. Important uncertainties remain, however, both in the parameterization of the small-scale process of bubble-induced gas exchange and in the large-scale representation of the physical processes that carry the bubble signature to depth. Here we summarize the results of the preceding sections, discuss the caveats that arise from this work, and offer suggestions for future refinements.

[46] We derived a parameterization for bubble-mediated gas transfer based on size-resolved bubble fields at different wind speeds calculated by a model of the turbulent oceanic boundary layer. The fluxes due to small collapsing bubbles and large partially dissolving bubbles are considered separately. Gas flux through bubbles is regressed against friction velocity which governs both bubble injection and bubble penetration depth. Bubble-induced surface equilibrium supersaturation rises rapidly with wind speed and is shown to be inversely related to temperature. These combined effects yield bubble-induced equilibrium supersaturation that is higher at high latitudes, offsetting the undersaturations that arise from surface cooling. The magnitude of this effect varies widely, however, among the different published parameterizations for the effect of bubbles. This uncertainty stems from the wide range of predictions for the wind speed dependence of bubble fluxes and their parameters.

[47] There are three primary uncertainties associated with our estimates of bubble-induced ocean ventilation. First, gas flux through bubbles ( $\mathcal{F}$ ) is determined by both bubble penetration and bubble entrainment. In the bubbly flow solutions used here, bubble penetration depth is controlled by ocean turbulence, while the absolute bubble amount is determined by bubble injection rate. Bubble injection rates applied here have been tuned to best match a series of laboratory and in situ measurements (see section 2). Nevertheless, uncertainties in bubble injection rate will lead to uncertainty in the resulting formulas (14) and (16). We are unable to quantitatively estimate the uncertainty in the measurements we fitted to and therefore the bubble injection rate used in the model. Both  $K_b$  and  $\mathcal{F}_C$  change proportionally with bubble injection rate, while  $\Delta_p$  is controlled by bubble penetration and do not change with bubble injection rate.

[48] Only the wind speed dependence of  $\Delta_{\text{eq}}$  is considered in this study. Recent studies have suggested that meteorological conditions besides wind speed, such as sea state and buoyancy flux, are additional governing factors for bubble injection and penetration [Woolf, 2005; Liang et al., 2012; Vagle et al., 2012]. These factors will also contribute to the variability of gas flux through bubbles and may be particularly important at high latitudes where turbulence is primarily driven by surface cooling.

[49] Second, our parameterization is based on simulations that include only  $\text{N}_2$  and  $\text{O}_2$ . It should therefore be considered accurate for gases with solubility similar to or less than those gases (e.g., Ar discussed extensively in section 4). However, the formulation may overestimate  $\Delta_{\text{eq}}$  for highly soluble gases such as  $\text{CO}_2$ . For bubbles that are small enough to have a relatively long life yet large enough to eventually burst at the ocean surface rather than completely collapsing, highly soluble gases may have equilibrated with

the surrounding water [Keeling, 1993; Woolf, 1993, 1997], while the less soluble but abundant gases ( $N_2$  and  $O_2$ ) have not. Addressing this possibility will require additional LES simulations that explicitly solve for  $CO_2$  dissolution.

[50] Finally, accurate determination of abyssal  $\Delta_b$  requires accurate representation of surface ocean conditions, especially at high latitudes during winter season where deep waters form. The use of circulation fields and meteorological conditions with variability at seasonal to synoptic scales is expected to provide a better estimate of bubble effect in the abyssal-dissolved gas concentration. Surface and circulation variability at interannual and longer time scales is also likely to be significant in abyssal gas concentrations.

[51] Advancement in these directions will require collaborative efforts from both observational and computational oceanographers. On the observation side, concurrent observations of subsurface bubbles populations, concentrations for multiple gases of different solubility, and ocean surface meteorological conditions have not been reported and can greatly improve our quantification of gas fluxes through bubbles. On the modeling side, the inclusion of highly soluble gases such as  $CO_2$  will allow a more robust estimate of bubble effects on these gases. Explicit simulation of the ventilation processes, including subduction and convection, over a wider range of meteorological conditions will be needed to identify the bubble effects that are obtained during the time periods of water mass formation.

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