On the calculation of air-sea fluxes of CO_2 in the presence of temperature and salinity gradients

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Abstract The presence of vertical temperature and salinity gradients in the upper ocean and the occurrence of variations in temperature and salinity on time scales from hours to many years complicate the calculation of the flux of carbon dioxide (CO_2) across the sea surface. Temperature and salinity affect the interfacial concentration of aqueous CO_2 primarily through their effect on solubility with lesser effects related to saturated vapor pressure and the relationship between fugacity and partial pressure. The effects of temperature and salinity profiles in the water column and changes in the aqueous concentration act primarily through the partitioning of the carbonate system. Climatological calculations of flux require attention to variability in the upper ocean and to the limited validity of assuming "constant chemistry" in transforming measurements to climatological values. Contrary to some recent analysis, it is shown that the effect on CO_2 fluxes of a cool skin on the sea surface is large and ubiquitous. An opposing effect on calculated fluxes is related to the occurrence of warm layers near the surface; this effect can be locally large but will usually coincide with periods of low exchange. A salty skin and salinity anomalies in the upper ocean also affect CO_2 flux calculations, though these haline effects are generally weaker than the thermal effects.

1. Introduction

Over the last two decades, there has been considerable debate over the importance of temperature values used in the calculation of global and regional CO_2 fluxes. The significance of precise temperatures can be readily understood from two facts. First, atmospheric and upper ocean CO_2 concentrations are almost in balance globally, with a net influx into the contemporary ocean of only approximately 2% of the diffusive exchange. Second, the efflux and influx depend on the fugacity or partial pressure of CO_2 (pCO_2) in the upper ocean and atmosphere, respectively, and the sensitivity of the fugacity in seawater is estimated at more than 4% per degree Kelvin temperature change [*Takahashi et al.*, 2009]. Thus, there appears to be a serious risk that mishandling temperature even slightly (i.e., biases of 0.1 K and less) can lead to substantial errors in calculated net flux. Given the significant role of the oceans in the global carbon cycle and the progression of ocean acidification, it is vital that ambiguities in the effect of temperature on CO_2 fluxes are resolved. That objective is the focus of this paper.

The careful treatment of temperature impacts strongly and debatably on calculated fluxes due to the variability and uncertainty of upper ocean temperatures, and due to the chosen treatment of the "cool skin" of the oceans. A recent climatology of CO_2 fluxes [*Takahashi et al.*, 2009] reports a global correction (increased oceanic uptake) of up to 0.28 Pg C yr^{-1} related to differences in sea surface temperature (SST) between standard climatological SST values and the SST measurements reported concurrently to oceanic pCO_2 measurements. The same climatology omits any correction for a cool skin, but other estimates have included a very large correction for this phenomenon.

The cool skin [e.g., *Donlon et al.*, 1999, 2002] is the phenomenon that the top millimeter or so of the upper ocean (the "thermal skin") is generally slightly cooler than the water below (the "mixed layer"). There have been several attempts to estimate the error in the net global CO_2 uptake if the thermal skin effect is neglected. Various studies reported an increased uptake of up to one third of the uncorrected uptake; for

example, *Robertson and Watson* [1992] reported a correction of ≈ 0.6 Pg C yr^{-1}), while *Van Scoy et al.* [1995] estimated ≈ 0.4 Pg C yr^{-1}.

McGillis and Wanninkhof [2006] have pointed out that the air-sea CO_2 flux is determined by a concentration difference across a very thin layer (much less than 1 mm) at the top of the ocean. As part of their analysis, they consider the thermal skin effect and note that only a fraction (perhaps only one tenth) of the temperature drop across the "thermal molecular boundary layer" or "thermal skin" will occur over the thickness of the "mass molecular boundary layer" that governs gas exchange. They infer that the significance of the thermal skin effect had been exaggerated by previous studies. *Zhang and Cai* [2007] followed the analysis of *McGillis and Wanninkhof* [2006] and calculated that the underestimate of the uptake due to ignoring the thermal skin effect was only ≈ 0.05 Pg C yr^{-1}, which, they calculated, would be almost exactly cancelled by an opposing haline effect associated with the salty skin of the ocean. More recently, *Woods et al.* [2014] provide a new estimate based on replacing a temperature at depth with a skin temperature, but retaining the original values of partial pressure.

There are a large number of thermal and haline effects that can potentially alter the air-sea flux of carbon dioxide (and other gases). In this paper, we provide a careful and detailed treatment of the thermal effects and also briefly discuss the haline effects. We review and adopt much of the framework provided by *McGillis and Wanninkhof* [2006]. We note three distinct mechanisms that link near-surface CO_2 concentrations, fluxes, and temperature (section 2 of this document). The significance of each mechanism to the different layers of the ocean is estimated, borrowing quantitative values from the illustrative example provided by *McGillis and Wanninkhof* [2006]. Thus, we concentrate upon the thermal profile of the upper ocean (section 3) and upon diffusive transfer in molecular sublayers immediately below the sea surface (section 4). We consider the effects of temperature trends and variation on CO_2 fluxes calculated from limited data collected over a few decades. A clarification to the correct inclusion of the "thermal skin effect" in gas flux calculations is summarized in section 5. As a result, we have revisited the significance of the thermal skin effect by considering particularly the error incurred if a sea surface temperature at any chosen depth in the upper meters of the ocean (variously defined and named as "Bulk SST" or "SSTdepth" in the literature) is used for all temperature and solubility calculations. An opposing effect is associated with ignoring the formation of a shallow diurnal warm layer (section 6), but this effect is regional and episodic.

We consider additional effects related to salinity (section 7). Generally, these analogous haline effects are smaller than the thermal effects, but worth including in a thorough calculation. The importance of climatological variation or secular trends in salinity and the sensitivity to the underlying cause is discussed. (This section draws on the specific experience of analyzing Arctic seas, reported in detail by *Land et al.* [2013]).

In section 8, we discuss the most important effects and the implications for calculating accurate air-sea flux climatologies for carbon dioxide. Finally, the important conclusions are summarized in section 9.

We have deliberately omitted another connection between temperature and gas fluxes: the coupling of heat and gas fluxes through irreversible thermodynamics. In principle that coupling also affects CO_2 fluxes, but we consider that *Doney* [1995] has adequately demonstrated that the effect is negligible for all practical purposes. We also assume that the gas at the interface will be in perfect equilibrium with the concentration in the lower atmosphere. That assumption requires neglect of vertical gradients in the marine atmospheric boundary layer and the "kinetic layer" immediately above the sea surface [see *Doney*, 1995, section 3]. Some effects of aqueous carbon chemistry are included, but we have assumed that hydration and dehydration rates are too low to significantly alter the transfer velocity of CO_2 [*Bolin*, 1960].

The intention of this paper is to provide a coherent account of the issues surrounding temperature and salinity handling, particularly as they relate to the calculation of air-sea CO_2 fluxes, regionally or globally. Studies applying this approach are published elsewhere [e.g., *Goddijn-Murphy et al.*, 2015].

2. Temperature and CO_2; Vapor Pressure, Solubility, and Isochemical Repartitioning

The top of the ocean is depicted schematically in Figure 1. Here we define an absolute interface (I) directly in contact with the atmosphere. Below that interface, we define two boundary layers: a mass boundary layer or molecular boundary layer (MBL) appropriate to the transfer of gases and salt (slightly different thicknesses
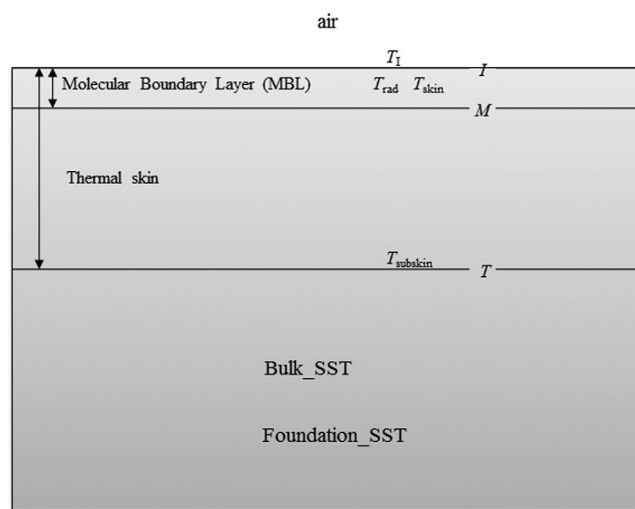
Figure 1. A schematic of the surface ocean, depicting the definition of the mass boundary layer (MBL), thermal skin, and various temperatures and depths. A "cloud" of temperature definitions including those used in this paper and those defined by GHRSST [*Donlon et al.*, 2007] are illustrated.

may be assigned to each solute, but we simplify this to a single definition) such that gradients of mass concentration associated with an air-sea disequilibrium are confined to this layer. Similarly, a thermal skin is defined such that temperature gradients associated with an interfacial heat flux are confined to this skin layer. The thermal skin is characteristically a factor of 10 thicker than the MBL. A number of additional depths and temperatures are shown schematically in Figure 1.

We include in Figure 1, an illustration of various temperatures used within this paper, but also the definitions promoted by the international GHRSST pilot project [*Donlon et al.*, 2007]. The GHRSST definitions are an end result of many years of research and discussion [e.g., *Donlon et al.*, 2002; *Ward et al.*, 2004] and attempt to provide practical definitions with a minimum of ambiguity. We use T for temperature and a subscript defining the position in the vertical profile. In most cases, these definitions follow closely the corresponding GHRSST parameter. The hypothetical temperature of the absolute temperature named SSTint by GHRSST is identified as T_I in this paper. We identify the temperature measured by an infrared radiometer as T_{rad}, which is the practical definition of the skin temperature, SSTskin. The temperature at the base of the MBL, T_M, has no direct equivalent in GHRSST, but will differ only slightly from SSTskin, because the MBL is typically less than 100 μm deep. Substantial thermal gradients are expected in a boundary layer in approximately the upper millimeter of the sea where turbulence is limited. We define T_T, equivalent to SSTsubskin in GHRSST terminology, for the temperature at the base of this thermal boundary layer. The thermal profile in the upper ocean below the top millimeter can be uniform, but more generally there will be thermal gradients [e.g., *Ward et al.*, 2004]. Traditionally, a Bulk SST, e.g., *Donlon et al.* [1999] was used for any temperature in the upper meters, but this practice and terminology is imprecise. We refer to the temperature at an unspecified depth as a Bulk SST, T_B, whereas GHRSST specifies the temperature at a measured depth, z, SSTdepth, or SST(z). The final temperature utilized in this paper is a foundation temperature, STTfnd. GHRSST define SSTfnd as the temperature of the water column free of diurnal variability, but it can be difficult to calculate that temperature from limited temperature data. A temperature measured during the nighttime is an imperfect substitute for SSTfnd but may be the most pragmatic choice.

For simplicity, we do not include salinity in Figure 1, but note here that the mass boundary layer applicable to salt diffusion is very similar to that applicable to dissolved gases. Haline effects will be considered further in section 7.

The net air-sea flux of a gas depends on the concentration difference of the volatile across the MBL; in the case of CO_2, we are concerned with the aqueous concentration of CO_2. If we write C_x as the aqueous concentration at a location x, then the direct air-to-sea flux across the sea surface, Fi, can be written

$$F_i = k_i (C_I - C_M) = k_i \, \Delta C \qquad (1)$$

where k_i is termed the interfacial transfer velocity and will be determined by the hydrodynamics of turbulent and molecular processes within the surface layers. We specify direct interfacial transfer since gas might also be transferred indirectly by bubble-mediated transfer, where gas transfers across the surface of bubbles [e.g., *Hare et al.*, 2004]. Therefore, the total flux, F can be defined by

$$F = F_i + F_b = k_i \, \Delta C + k_b \, \Delta C_b \qquad (2)$$

We will largely ignore the bubble-mediated flux hereafter but include it above for completeness and note also that the temperatures and salinity values that should be used in the calculation of the bubble-mediated flux, F_b, will in principle differ from those described below for the calculation of the interfacial flux, F_i.

We show the correct calculation of the concentration difference and gas flux using appropriate temperatures and explain the consequences of assigning the wrong temperature. The following five subsections break down the calculation as follows:

1. calculation of the exact fugacity at the interface,
2. calculation from (1) of the concentration of aqueous CO_2 at the interface,
3. calculation of the concentration at the base of the MBL,
4. calculation of the interfacial transfer velocity, and
5. calculation of the interfacial flux and errors resulting from the wrong temperature.

Finally, we conclude section 2 with subsections (6) summarizing the thermal effects for carbon dioxide (CO_2) and other gases, and (7) explaining the origin of a common misconception.

2.1. Calculation of Interfacial Fugacity, f_I

The concentration at the base of the atmosphere is calculated by the method of *McGillis and Wanninkhof* [2006]. In this method, the partial pressure of CO_2, at sea level, p_{CO_2}, is calculated from values for the dry molecular fraction of CO_2 in the atmosphere, X_{CO_2}, the atmospheric pressure, P, and the saturation water vapor pressure, p_{H2O} thus,

$$p_{CO_2} = (P - p_{H_2O})X_{CO_2} \tag{3}$$

The saturation water vapor pressure is dependent on temperature and salinity and should be calculated using the interfacial water temperature, T_I, and interfacial salinity, S_I (using a formula from *Weiss and Price* [1980]; see *McGillis and Wanninkhof* [2006, equation A1]).

Since saturated vapor pressure is sensitive to temperature, an error in interfacial temperature will affect the calculation of the partial pressure of CO_2. The magnitude of the effect is temperature dependent and should be calculated carefully, but for illustration we can use the example provided by *McGillis and Wanninkhof* [2006, Figure 1 and table therein] that implies an sensitivity of −0.2%/K of the interfacial concentration to an error in the applied temperature by this mechanism alone (i.e., if the actual interfacial temperature was 15°C, but it was assumed to be 16°C, the surface fugacity would be underestimated by 0.2% as a result of overestimating vapor pressure and thus underestimating the partial pressure of CO_2).

Having calculated a partial pressure, it is thorough to apply the distinction between fugacity and partial pressure (using the fugacity correction given by *Weiss* [1974]; see *McGillis and Wanninkhof* [2006, equation A5]). This equation again includes interfacial temperature and strictly speaking is an additional mechanism of sensitivity to the interfacial temperature, but it is very small and we group it with the vapor pressure effect to give a combined effect on interfacial fugacity that is rounded to −0.2%/K.

In summary, we define a sensitivity of the interfacial fugacity to temperature, Φ_1, calculated as

$$\Phi_1 = \partial \ln f_I / \partial T \approx -0.2\%/K \tag{4}$$

2.2. Calculation of Interfacial Concentration, C_I

The aqueous concentration of CO_2 in the interface, C_I, is then calculated from the solubility, K_0, and the interfacial fugacity, f_I, thus:

$$C_I = K_0 f_I \tag{5}$$

The solubility, K_0, is temperature and salinity dependent. Unfortunately, the formulae available for calculating solubility are quite imprecise. For example, *McGillis and Wanninkhof* [2006, Figure 5] show that the solubilities predicted by *Weiss* [1974] and by *Li and Tsui* [1971] typically differ by 2% in warm seawater. This uncertainty introduces an inevitable ambiguity in the estimate of surface fluxes. A substantial error may occur by not consistently using the same formula at both the interface and within the water column and therefore this should certainly be avoided.
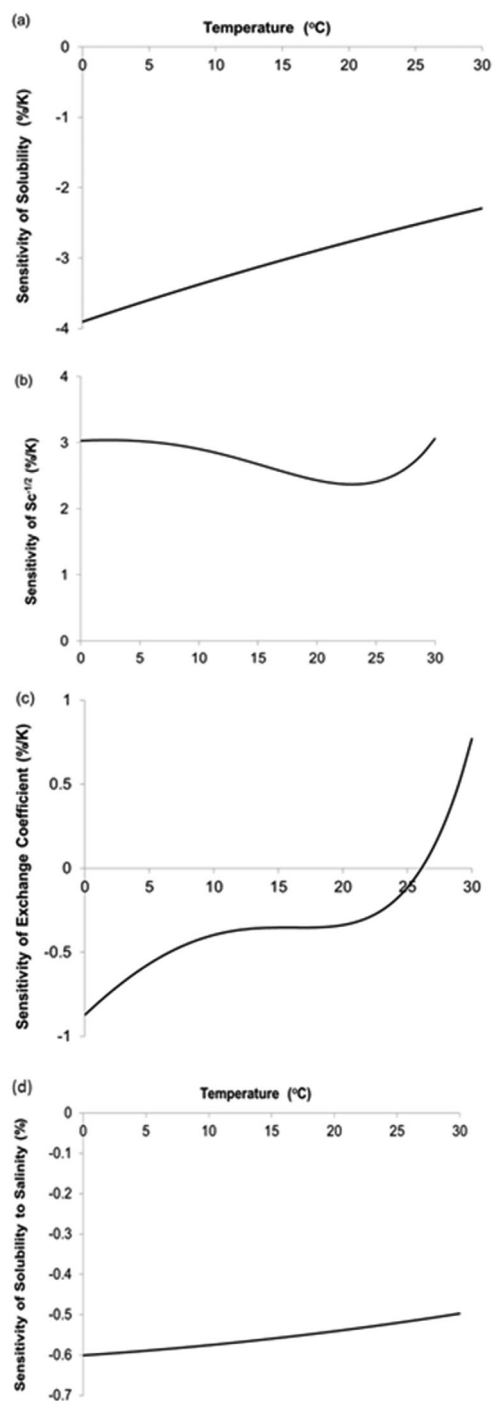
Figure 2. Sensitivity of factors affecting the calculation of the air-sea flux of carbon dioxide as a function of water temperature. (a) Sensitivity of the solubility of carbon dioxide to temperature at S = 35. Sensitivity is defined as $\partial \ln K_0 / \partial T$ and calculated according to the relationship of *Weiss* [1974]. (b) Sensitivity of $Sc^{-1/2}$ to temperature at S = 35, where Sc is the Schmidt number of carbon dioxide. Sensitivity is defined as $\partial \ln(Sc^{-1/2}) / \partial T$ and is calculated according to the formula of *Wanninkhof* [1992]. (c) Sensitivity of $K_0 Sc^{-1/2}$ to temperature at S = 35. Sensitivity is defined as $\partial \ln(K_0 Sc^{-1/2}) / \partial T$. (d) Sensitivity of the solubility of carbon dioxide to salinity as a function of temperature. Sensitivity is defined as $\partial \ln K_0 / \partial S$ and calculated according to the relationship of *Weiss* [1974].

Since solubility depends on temperature and salinity, the calculation of interfacial concentration using solubility introduces a bias resulting from mishandling the temperature or salinity in the solubility formula. The sensitivity to solubility is typically the largest effect of temperature on the calculated concentration gradient. As a first illustration, we can use again the example provided by McGillis and Wanninkhof that implies a sensitivity of −2.5%/K of the interfacial concentration to an error in the applied temperature by this mechanism alone, or −2.7%/K as a combined effect on the calculated interfacial concentration with the "effect on fugacity" described in section 2.1. A more precise calculation depends on taking the derivative of the solubility with respect to temperature, for which we chose the formula for solubility given by *Weiss* [1974]. The result for a fixed salinity of 35 is shown in Figure 2a. The value of −2.5%/K is typical for fairly warm water (coinciding with the more exact value for a temperature between 25 and 26°C) but the sensitivity rises to almost −4%/K at 0°C making correct handling of this effect particularly important in cold Polar waters.

In summary, we define a sensitivity of the interfacial solubility to temperature, Φ_2, calculated as

$$\Phi_2 = \partial \ln K_0 / \partial T \approx -2.5\%/K \qquad (6)$$

That concludes the procedure to calculate the correct interfacial concentration.

2.3. Calculation of Concentration at the Base of MBL, C_M

When a sample of seawater is subjected to a change of temperature, the aqueous concentration of CO_2 is changed. The equations of carbonate chemistry imply that while some properties may be conserved (notably "total dissolved inorganic carbon" and "alkalinity" in gravimetric units) the aqueous concentration and partial pressure of CO_2 will change under a change in temperature. Variations in temperature within the upper ocean and the nature of the changes implied will be explained in section 3. This point is also relevant to processing of in situ CO_2 data [*Goddijn-Murphy et al.*, 2015]. For now, we review only the implied sensitivity of concentration to temperature resulting from the behaviour of carbonate chemistry.

The most common assumption for such calculations is that alkalinity and total dissolved inorganic carbon are conserved (an "isochemical change"), but aqueous CO_2 is typically increased by warming, or decreased by cooling due to a repartitioning of the species of the carbonate system. For clarity, it is better to calculate the effect on concentration directly. However, it is also valid to calculate an effect on fugacity first and
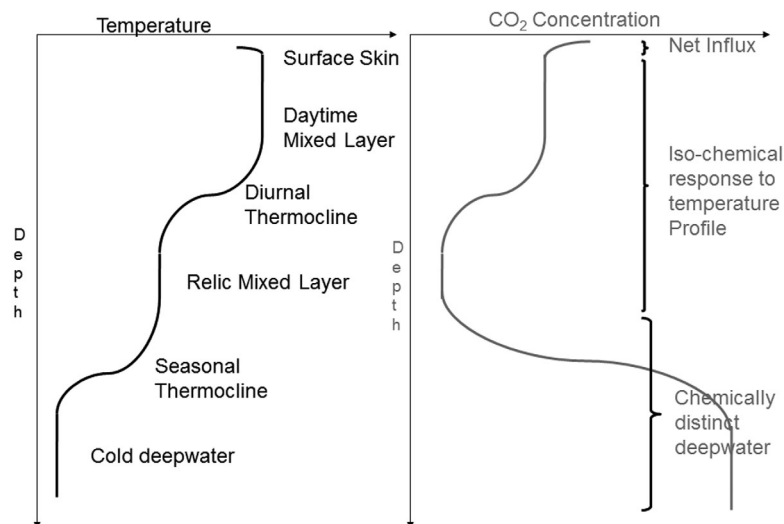
Figure 3. Schematics of the vertical profiles of temperature and aqueous CO_2 concentration. Temperature profile in black, CO_2 in gray. Total dissolved inorganic carbon (T_{CO_2}) and alkalinity (T_{Alk}) are not shown explicitly for simplicity, but we label an upper portion of the profile where T_{CO_2} and T_{Alk} may be constant, and a lower portion where T_{CO_2} and T_{Alk} will usually be higher than in the upper ocean.

then calculate the corrected concentration. Thus, for a δT increase in water temperature, an increase of ~4% δT in fugacity is first calculated, from which a 2.5% δT change due to solubility can be removed to arrive at ~1.5% δT increase in concentration from the equations of carbonate chemistry. This effect was noted by *Hare et al*. [2004] and included in their equation (12), but with some confusion in their definition of δT.

A widely applied correction for thermally induced changes in carbonate chemistry is based on a measurement of fugacity change of North Atlantic seawater in isochemical conditions by *Takahashi et al*. [1993]. The correction can be expressed either in a more exact temperature-dependent form or in a simpler form:

$$\partial \ln p_{CO_2}/\partial T(^\circ C) = 0.0433 - 8.7 \times 10^{-5} \, T(^\circ C) \tag{7}$$

$$\partial \ln p_{CO_2}/\partial T(K) = 0.0423 \tag{8}$$

The sensitivity does vary with temperature and *Takahashi et al*. [2009] chose to use the former, more precise expression for corrections between the equilibrator and in situ, but used the simpler form for an estimate of the "error due to undersampling" (which is related to the issue of the in situ temperatures being unrepresentative of climatology) [*Goddijn-Murphy et al*., 2015]. The second version, equation (8), has been more commonly used historically and is still in common use, for example for corrections from equilibrator temperature and in situ in the construction of the SOCAT database [*Wanninkhof and Thoning*, 1993; *Pfeil et al*., 2013]. Equation (7) is likely to be more accurate. *Takahashi et al*. [2009] state that since the typical temperature changes in an underway system are small the error in using equation (8) is negligible. We note that it is nonetheless an identifiable systematic bias that should be avoided where practical. *Goddijn-Murphy et al*. [2015] show that it is practical to "retrieve" the original equilibrator values from most data records and then apply equation (7) throughout.

McGillis and Wanninkhof [2006] recommend that the correction is made directly to concentrations and that the full equations of the carbonate system are used [*Mehrbach et al*., 1973; *Lewis and Wallace*, 1998; *Dickson and Millero*, 1987]. That is undoubtedly a more thorough method, but it does require additional information on total dissolved inorganic carbon and alkalinity. *McGillis and Wanninkhof* [2006] point out methods that ignore the varying chemistry of seawater (note the report of *Takahashi et al*. [1993] is based solely on a North Atlantic surface water sample) will neglect the true variability in the isochemical changes. They credit *Copin-Montegut* [1988] and *Goyet et al*. [1993] with showing that "the temperature dependence is a function of temperature, salinity and T_{CO_2}/T_{Alk} ratio." *McGillis and Wanninkhof* [2006, Figure 3 and associated text] report the sensitivity of fugacity to temperature may vary from 5.3% at 0°C to 3.7% at 30°C (in part a response to the associated latitudinal gradient in total dissolved inorganic carbon, T_{CO_2}). The temperature-dependent version

of the formula based on *Takahashi et al.* [1993], equation (7), trends in the same direction, but the trend is weaker, varying from 4.33% at 0°C to 4.07% at 30°C.

It may be appropriate to use available measurements of T_{CO_2}, and T_{Alk} and complete chemical calculations, however, most analyses are limited by data availability and there are some remaining uncertainties due to substantial differences in subsidiary equations [*McGillis and Wanninkhof*, 2006; *Mehrbach et al.*, 1973; *Dickson and Millero*, 1987; *Goyet et al.*, 1993]. Therefore, we propose that equation (7) is the pragmatic choice.

In summary, we define a sensitivity of the subsurface aqueous concentration to temperature, Φ_3, calculated as

$$\Phi_3 = \partial \ln C_w / \partial T \approx +1.5\%/K \tag{9}$$

2.4. Calculation of Interfacial Transfer Velocity, k_i

The transfer of an unreactive gas across the MBL is dependent on molecular and turbulent processes. Carbon dioxide can be treated as unreactive for the time scales appropriate to transfer processes within MBL. There is both theoretical and experimental support for the molecular properties of the water and dissolved gas entering into the transfer velocity through the Schmidt number, Sc, defined as the ratio of the kinematic viscosity, υ, and the molecular diffusion coefficient of the dissolved gas, D, thus

$$Sc = \upsilon/D \tag{10}$$

It is also often proposed [e.g., *Hare et al.*, 2004] that the interfacial transfer velocity will be proportional to the inverse square root of the Schmidt number, Sc. It is also common to rewrite the flux equation in terms of a transfer velocity at a reference Schmidt number, for example k_{660} represents a value of transfer velocity for a Schmidt number of 660, and the flux equation is as follows

$$F_i = (660/Sc)^{0.5} k_{660} (C_I - C_M) = (660/Sc)^{0.5} k_{660} \Delta C \tag{11}$$

Temperature and salinity enter into the calculation of Sc since both kinematic viscosity and diffusion constants are temperature and salinity dependent. Most significantly, the Schmidt number of a dissolved gas will generally decrease quite rapidly with temperature. The increase with temperature of $Sc^{-1/2}$ (and by implication the increase in k_i) for carbon dioxide can be calculated from published expressions for the temperature dependence of Sc individually, or its constituents (e.g., υ and D). A cubic expression for the dependence of the Schmidt number of CO_2 in seawater as a function of water temperature (salinity variations are neglected) [*Wanninkhof*, 1992] is most widely used. That expression is used to calculate the sensitivity of $Sc^{-1/2}$ to temperature, which we show in Figure 2b. A rough approximation for the sensitivity of $Sc^{-1/2}$ to temperature is approximately 2.5%/K, but there is some substantial variation as apparent in Figure 2b. A numerical scheme described by *Johnson* [2010] is probably more accurate and gives Schmidt numbers that differ by up to a few percent from the cubic expression. Since temperature will vary within the depth profile that interfacial processes occur (Figure 1), it is not entirely obvious what temperature to use in the calculation of Sc and k_i, but a value for the interface is clearly preferable to a deep value (i.e., T_I is preferred to T_B or SSTdepth).

In summary, we define a sensitivity of the interfacial transfer velocity to temperature, Φ_4, calculated as

$$\Phi_4 = \partial \ln k_i / \partial T = \partial \ln(Sc^{-0.5}) / \partial T \approx +2.5\%/K \tag{12}$$

2.5. Calculation of Errors in the Interfacial Flux, F_i

Here we consider the effects of mistaken assignments of temperature on the calculated interfacial flux, F_i, i.e., we will calculate the error, dF_i and the fractional error, dF_i/F_i where a temperature $T_x + dT_x$ is assigned instead of the correct temperature T_x. In particular, we will consider the effects of errors in T_I and in T_B as implied by the four preceding subsections.

As described in sections. 2.1, 2.2, and 2.4, the calculation of the fugacity and concentration at the interface precisely requires the interfacial temperature, T_I, while the calculation of the transfer velocity might also reasonably use T_I. For simplicity, we will calculate effects of an error dT_I in each calculation using the simple approximations to the sensitivity described in the preceding subsections. We designate the true flux as F_i at

the true temperature T_I and the erroneous flux due to using an interfacial temperature $T_I + dT_I$ as $F_i + dF_{iI}$. It follows from equation (1) that the erroneous flux can be written as

$$F_i + dF_{iI} = k_i(1 + \Phi_4 dT_I) \ [C_I + (\Phi_1 + \Phi_2) \ C_I \ dT_I - C_M] \tag{13}$$

$$F_i + dF_{iI} = k_i(C_I - C_M) + k_i \ [\Phi_4 dT_I(C_I - C_M) + (\Phi_1 + \Phi_2) \ dT_I \ C_I] \tag{14}$$

Where the three sensitivities Φ_1, Φ_2, and Φ_4 to interfacial temperature have been defined and explained in sections 2.1, 2.2, and 2.4, respectively. In equation (13), we have represented the individual errors to first order only, and in the second version, equation (14), a further second-order term is discarded. In equation (14), we have separated each side of the equation into the true value (the first term) and an error value (the second term). Subtracting the true values, the value of the error terms can be written:

$$dF_{iI} = dT_I k_i [\Phi_4(C_I - C_M) + (\Phi_1 + \Phi_2) \ C_I] \tag{15}$$

The fractional error in flux can be written:

$$dF_{iI}/F_i = dT_I[\Phi_4 + \ (\Phi_1 + \Phi_2) \ C_I/(C_I - C_M)] \tag{16}$$

Substituting the approximate values described in sections 2.1, 2.2, and 2.4, we find:

$$dF_{iI}/F_i = dT_I[2.5\% + (-0.2\% + -2.5\%) \ C_I/(C_I - C_M)] \tag{17}$$

More accurate values of the third and first percentages can be read from Figures 2a and 2b. The sensitivity of the transfer velocity to temperature (section 2.4; Φ_4) increases the size of the net flux slightly for a reasonable positive value of dT_I. By contrast, the phenomena described in sections 2.1 and 2.2 (Φ_1 and Φ_2) affect only the downward flux and both reduce that downward flux slightly for a positive dT_I. Their effect on the net flux is proportionally greater in near-saturation conditions ($C_I \sim C_M$). In global terms, carbon dioxide is almost in balance between atmosphere and ocean and more generally the magnitude of the ratio $C_I/(C_I - C_M)$ will be much greater than 1 at most locations on the sea surface. Those facts are highly pertinent to the relative importance of the phenomena. It is clear that the solubility effect (represented by Φ_2; section 2.2) will usually be the most important effect. The vapor pressure and fugacity-partial pressure effects (jointly represented by Φ_1; section 2.1) are an order of magnitude less important for carbon dioxide than the solubility effect. The Schmidt number effect (Φ_4; section 2.4) will usually be less important than the solubility effect but may be of similar importance in special circumstances, for example if $C_M \ll C_I$.

We consider next the effect of an error in the flux, dF_{iM}, associated with an error dT_M in the temperature, T_M, at the base of the MBL. As described in section 2.3, there is a thermal effect on the aqueous concentration of CO_2 related to partition of the carbonate system with a sensitivity of approximately 1.5%/K, which we designate Φ_3. Following a similar analysis to the interfacial effects, we can write the following equations

$$dF_{iM} = -dT_M k_i \Phi_3 \ C_M \tag{18}$$

$$dF_{iM}/F_i = -dT_M \Phi_3 \ C_M/(C_I - C_M)] \tag{19}$$

Substituting the approximate value of 1.5%/K for Φ_3 gives

$$dF_{iM}/F_i = -dT_M[1.5\% \ C_M/(C_I - C_M)] \tag{20}$$

This subsurface effect of repartitioning is comparable in magnitude for carbon dioxide to the interfacial effects described by equations (15)–(17) and therefore both sets of effects require close attention. It is worth noting the signs of the effects. For a common error in temperature ($dT_I = dT_M$), such as may occur for a general misassignment of temperature, the solubility and repartitioning effects reinforce each other, potentially resulting in a substantial error in the calculated flux.

2.6. Summary of Effects and Generalization to Other Poorly Soluble Gases
In Table 1, we summarize the thermal effects on carbon dioxide fluxes, identifying their physical origin, the scaling of the flux error with concentration or concentration difference and the scaling factor. We include also a column describing the relevance to other gases, particularly to the simple case of gases that are poorly soluble, unreactive and ideal. One of the major effects for carbon dioxide, repartitioning (section 2.3; Φ_3), is a peculiarity of the carbonate system and is ineffective for unreactive gases. A small effect impacting

Table 1. Thermal Effects on the Calculation of Air-Sea Gas Fluxes (Carbon Dioxide and Other Poorly Soluble Gases), Notation, and the Significance of Each

Origin of Effect	Subsection and Scaling	Scaling Parameter	Approximate Scaling Factor (CO_2)	Effect on Unreactive, Ideal Gases
Vapor pressure and nonideality	Section 2.1, Φ_1	C_I	$-0.2\%/K$	Similar, but smaller effect related to nonideality vanishes
Solubility	Section 2.2, Φ_2	C_I	$-2.5\%/K$	Variable, but typically most important
Carbonate chemistry	Section 2.3, Φ_3	C_M	$1.5\%/K$	Not applicable
Schmidt number	Section 2.4, Φ_4	$C_I - C_M$	$2.5\%/K$	Variable, but typically significant

the relationship of partial pressure and fugacity, section 2.1, is a product of nonideality, but the greater part of Φ_1 is unrelated to the gas, as it arises from vapor pressure and therefore Φ_1 will be similar for all gases. The sensitivities Φ_2 (solubility; section 2.2) and Φ_4 (Schmidt number; section 2.4) are generally relevant but need to be evaluated from the physical constants of the gas of interest.

2.7. Explaining a Misconception

It is occasionally stated in the literature that errors or changes in temperature barely affect the calculation of flux since effects on solubility and Schmidt number cancel. The origin of this observation can be understood by rewriting the interfacial flux equation in terms of fugacity or partial pressure difference instead of concentration difference, that is

$$F_i = K_0(660/Sc)^{0.5}k_{660}(f_I - f_M) = K_0(660/Sc)^{0.5}k_{660}\Delta f \tag{21}$$

In that equation, the product $K_0 Sc^{-0.5}$ appears and contains the product of solubility and the inverse square root of Schmidt number, each of which is sensitive to temperature (see Figures 2a and 2b). The sensitivity of the product of the two terms is calculated and presented in Figure 2c. It is apparent from the figure, that the two terms do approximately (though not precisely) cancel and at a first glance equation (21) and Figure 2c may suggest a low sensitivity to temperature. Thus, equation (21) represents the origin of the misconception. However, that interpretation depends on assuming the fugacity difference is correct, or specifically it will not be affected by errors in temperature. The explanations in the preceding subsections should make it clear that the assumption is unreasonable. Equation (21) is useful in suggesting that it is the miscalculation of the disequilibrium between atmosphere and ocean that is most significant, while miscalculations of an exchange coefficient are relatively unimportant. That insight again emphasizes that the significance of thermal effects to global carbon dioxide is greatly amplified by the near balance of CO_2 between atmosphere and ocean, since that situation renders errors in the calculation of the small imbalance most critical.

Equation (21) is invalid in the case of vertical temperature gradients and should be avoided. The main flaw in the equation is an unresolvable ambiguity in the temperature required for the calculation of solubility. It is far safer to write the gas flux equation in terms of concentration difference (equation (1)), but it is reasonable to write each concentration as a product of solubility and fugacity, provided the appropriate solubility is associated with each fugacity. Thus, a corrected version of equation (21) can be written:

$$F_i = k_i(K_{0I}f_I - K_{0M}f_M) = k_{660}(660/Sc)^{0.5}(K_{0I}f_I - K_{0M}f_M) \tag{22}$$

It is important to note here that it is not sufficient to use the correct values of temperature in the calculation of the solubility and transfer velocity within equation (22), but the fugacities must also be calculated correctly for each side of the MBL, which in general will require manipulation of the original partial pressure or fugacity data.

3. Profiles, Distribution, and Variation

Temperature, salinity, and parameters of the CO_2 system all vary in the ocean. As a prerequisite for inferring general values of properties from local and sparsely sampled measurements of CO_2 and other properties, we need to understand these distributions and how variations of carbonate parameters are related to variations of other oceanic properties. The importance of dealing adequately with temperature variability in the upper ocean can be understood by reference to *Takahashi et al.* [2009, section 6.4.4], where they describe a

correction of up to -0.28 Pg C yr^{-1} related to temperature discrepancies between a standard climatological SST and SST measurements concurrent to oceanic pCO_2 measurements. It is particularly important to understand when an assumption of "isochemical repartitioning" is reasonable.

Standard texts on chemical oceanography [e.g., *Emerson and Hedges*, 2008; *Williams and Follows*, 2011] explain the centrality of total dissolved inorganic carbon (T_{CO_2}) and alkalinity (T_{Alk}) to the understanding of carbonate chemistry in the oceans. T_{CO_2} and T_{Alk} are useful parameters of the carbonate system partly because they are conserved properties (in gravimetric units) with respect to some processes, including changes in temperature or pressure. T_{CO_2} conservation represents a mass conservation, while T_{Alk} conservation represents charge conservation. Most studies of thermal effects (such as described in section 2.3) rely on T_{CO_2} and T_{Alk} being conserved properties and consider the change in aqueous CO_2 resulting from a temperature change at constant chemistry (or "isochemical repartitioning"). It must be understood that many processes do not conserve T_{CO_2} or T_{Alk}. For example, *Williams and Follows* [2011, Figure 6.16], identify organic matter formation, calcification, and dilution as processes that change both T_{CO_2} and T_{Alk}. Air-sea gas exchange conserves charge and T_{Alk} but changes T_{CO_2} over a long period of time. In the fine detail, T_{CO_2} and T_{Alk} conservation will rarely be exact in the natural environment. For example, *McGillis and Wanninkhof* [2006, Figure 2] note a diurnal change in T_{CO_2} (after a report by *McGillis et al.*, 2004] that contributes (along with thermal changes) to the diurnal change in fugacity. In modelling and interpolating CO_2 measurements, some pragmatic assumptions are often necessary, which may include where sensible an assumption of constant chemistry. In the following, we will consider when and where that assumption can be justified.

Temperature varies in the vertical; a fairly common example is described schematically in Figure 3. The water at the sea surface is typically cooler than below, increasing with depth over the first millimeter. The water in at least a few meters below (and more often over tens of meters) is usually actively mixed by the action of the wind and thus temperature, salinity, carbonate parameters, and most other properties are almost constant in the vertical. In Figure. 3, we show a fairly common but minority situation where there is a relatively shallow, actively mixed warm layer that has separated from deeper water due to surface warming (a diurnal layer; generally associated with strong daytime insolation combined with light winds). This layer will also usually be slightly more saline than the deeper water due to evaporation, but this may be counteracted by rainfall. A rarer phenomenon is a freshwater "pool" at the surface associated with high rainfall and gentle winds [*Soloviev and Lukas*, 1996]. Diurnal warm layers are fairly common where insolation is high and the wind is fairly weak but will usually breakdown each night to form a more typical deeper mixed layer. Figure 3 depicts a "relic mixed layer" below the diurnal warm layer and extending to either a seasonal or permanent thermocline. More often this layer will extend to the sea surface (excepting the cool skin). When mixed, the entire water column is returned to a foundation temperature. Generally, any nighttime measurement within the water column measures foundation temperature approximately (but note the more precise definition of foundation temperature favored by GHRSST as described in section 2) [*Donlon et al.*, 2007]. During the daytime, a measurement will only retrieve a reasonable approximation to the foundation temperature if it is below any daytime warming. Therefore, some sea surface temperature climatologies use only nighttime data to calculate a foundation temperature. Since changes in T_{CO_2} and alkalinity within 1 day are usually miniscule it is usually reasonable to assume that these properties are uniform within this layer. Similarly, with some caution, we might approximate that within any reasonable geographical area and time period, mixed layer T_{CO_2} and T_{Alk} are invariant and the variations in the fugacity and concentration of CO_2 are primarily isochemical (strong variations in salinity may be an exception as discussed in section 7). Thus, we can make a limited justification for taking numerous samples of measured CO_2 in a single calendar month and geographical area (say, a $1° \times 1°$ grid square) and correcting each to the climatological temperature of that area and time. The sample mean of the corrected concentrations can be assumed to be an unbiased estimator of the true mean, while the sample standard deviation and standard error will reflect a number of phenomena including some chemical variation.

Below the seasonal mixed layer, the water is necessarily denser, which may be due to salinity rather than temperature. In Figure 3, we depict cooler water below the seasonal mixed layer, but in many cases the water is warmer but more saline. This water is physically and chemically distinct. The total DIC, T_{CO_2}, and especially the alkalinity, T_{Alk}, are almost invariably higher in the deeper water. The concentration of aqueous CO_2 will also depend on temperature and salinity. Figure 3 depicts an example where the net effect is higher concentration in the deep water, but the important thing is that the deeper water is chemically

distinct. Where there is an exchange with this deeper water (e.g., entrainment of thermocline water by a deepening mixed layer), the change in mixed layer properties will not be isochemical in nature and no such assumption is tenable. For example, both the seasonal and interannual variations in upper ocean properties will normally involve such exchange and applying an assumption of constant chemistry would be unreasonable. Similarly, exchange between atmosphere and ocean is considerable on seasonal time scales and this exchange also represents changes in the upper ocean that are not isochemical. The limits over which isochemical transformations are practical are apparent from studies of the seasonality of carbonate chemistry [e.g., *Brostrom*, 2000]. It may be pragmatic to neglect departures from constant chemistry within a single month (or at least, to treat each sample within a given month transformed by an isochemical correction to the climatological temperature of that month as equally representative). Applying isochemical transformations over more than 1 month cannot be justified.

4. The Thermal and Mass "Skins"

McGillis and Wanninkhof [2006] have noted that there is an important distinction between the transfer of mass and heat in the upper millimeters of the ocean due to their very different molecular diffusion constants in seawater. Gases and solutes (including salt) vary significantly but generally their molecular diffusivity is of the order of 100 times less than that of heat. A very thin layer at the sea surface largely controls gas transfer due to the suppression of turbulence in that layer. The first models of air-sea transfer of CO_2 [*Bolin*, 1960; *Broecker and Peng*, 1974] represented the transfer by a stagnant layer model where gas transfer was only possible by molecular transfer across a very thin layer at the sea surface, while transfer was exceedingly rapid due to turbulent mixing beneath that stagnant layer. In the stagnant layer model, in a steady state, there should be a linear gradient across the stagnant layer and constant concentration below. The thickness of the stagnant layer, L, should be related to the molecular diffusivity, D, and transfer velocity, k_w, by $L = D/k_w$. Early estimates of the transfer velocity of gases implied a global mean stagnant layer thickness of 30–35 μm [*Bolin*, 1960; *Broecker and Peng*, 1974]. Bolin noted that the time to diffuse across a stagnant layer relative to the hydration time for CO_2 in seawater was highly significant to the transfer velocity of CO_2. The time scale for diffusion across a stagnant layer must be $\sim L^2/D$; which will be of the order of 1 s for $D \sim 10^{-9}$ m^2/s; while hydration and dehydration result in equilibration in $\approx$30 s for seawater at 25°C, rising to a few minutes in cold water [*Johnson*, 1982; *Emerson and Hedges*, 2008]. *Bolin* [1960] reasoned that as the hydration rate is relatively slow, transfer is limited by the diffusion rate of aqueous CO_2 and the transfer velocity is slow (similar to unreactive gases). If all the reactions between carbonate species were effectively instantaneous then the diffusion of all carbonate species would contribute and the transfer velocity of CO_2 would be much faster.

The stagnant layer thickness remains a useful concept, but the stagnant layer model is largely discarded. One reason for that neglect is the finding that the transfer velocities of unreactive tracers do not vary with a simple inverse of diffusivity, but $k_w \sim D^{1/2}$ (or $Sc^{-1/2}$) is a better approximation. This approximation extends to heat in the surface skin and it is found that heat is transferred approximately 10 times quicker than CO_2. Inputting the measured transfer coefficients back into the calculation of an "equivalent stagnant layer thickness," it follows that the stagnant layer thickness for heat is approximately 10 times greater than that for CO_2. However, the paradigm for concentration and temperature gradients in the surface skin has also shifted. The discovered diffusivity dependence is attributed to a gradual "hand over" across the molecular boundary layers between purely molecular diffusion at the interface and dominant turbulent transport. Various models of this process are current, but they generally imply a stochastic process and inhomogeneous concentration or temperature at any depth within the skin. Nevertheless, it is possible to consider an average temperature and concentration profile, which will be curved as the hand over to turbulent transport progresses further as the interface recedes. The average profiles for CO_2 and temperature are shown schematically in Figure 4. Though we expect a ratio in thickness of approximately 10, the figure is not drawn to scale, rather the mass boundary layer is enlarged sufficiently to show it clearly.

The layering of the upper ocean has been introduced in Figure 1 and defined in section 2, with reference to the GHRSST definitions of sea surface temperature [*Donlon et al.*, 2007]. Key depths are depicted in Figure 4. "M" signifies the base of the mass boundary layer and "T" the base of the thermal boundary layer. "I" determines the precise interface between air and sea. Interfacial concentration and
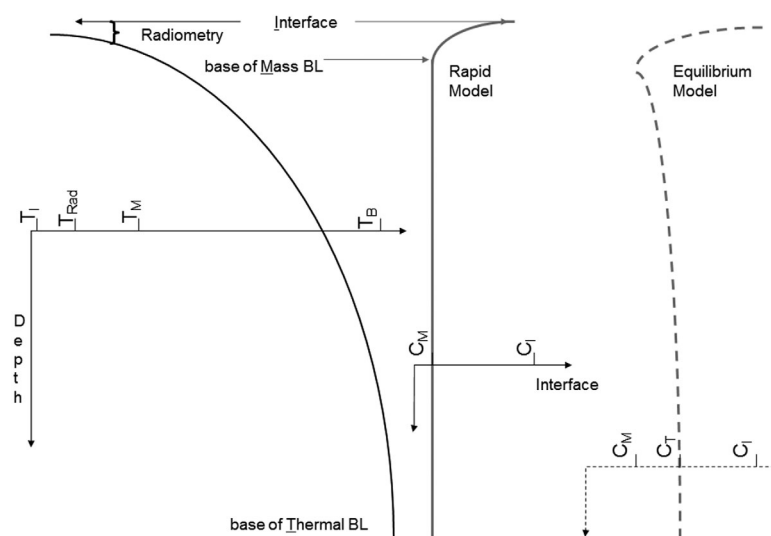
Figure 4. Schematics of vertical profiles within the surface microlayer. Temperature profile in black, CO_2 in gray. Two CO_2 profiles are shown on the same concentration scale, each appropriate to one of two limiting cases described in the text. The full gray curve describes the profile for a "rapid model," while the dashed gray curve describes the profile for an "equilibrium model."

temperature is a useful mathematical concept, but quite difficult to define physically and impractical to measure. A more practical value of sea surface temperature is the radiometric temperature, T_{rad}. Since infrared radiation is absorbed by a thin layer of seawater, the infrared radiation from the sea surface into the atmosphere is emitted by a very thin layer, $\sim$20 μm thick. Usually T_{rad} (or SSTskin, in GHRSST terminology) is considered to be an adequate practical alternative to the abstract concept of interfacial temperature, T_I (or SSTint). Since the radiometric thickness is not much less than the equivalent stagnant layer thickness for mass, T_{rad} may also be a pragmatic substitute for T_M. T_{rad} is not an adequate substitute for the temperature at the base of the thermal skin. It must also be noted that some satellite radiometric temperature data sets, while detecting the temperature variation at the skin, are actually calibrated to temperature at depth. Therefore, it is important to use values of T_{rad} that are calibrated (or corrected back to) skin temperatures.

The profile in temperature or gas concentration is often presented as a linear gradient near the surface and a uniform value below, corresponding to a stagnant layer and a turbulent mixed layer, respectively. This simple view can be useful but ignores the rejection of stagnant layer models in recent years. A curved profile is implicit in more realistic models of air-sea exchange, but the most appropriate model remains open to debate [e.g., *Fairall et al.*, 2000; *Atmane et al.*, 2004; *Asher et al.*, 2004]. Here we infer a curved profile in temperature and this is depicted in Figure 4, but we do not attempt to define the profile exactly.

There is some ambiguity in the precise form of the averaged concentration gradient (full and dashed gray curves in Figure 4). An air-sea flux is driven by a concentration difference across the mass boundary layer and in both versions of the concentration profile, we depict the main concentration difference between "I" and "M" (in this case decreasing from the surface down, consistent with a net flux into the sea). A significant gradient in total DIC is not expected below "M," since this water should be "well mixed." However, there is expected to be a temperature gradient between "M" and "T" and thus "isochemical repartitioning" implies that at equilibrium there should be a constant concentration of CO_2 below the base of the thermal boundary layer but a progressively lower concentration in the cooler water above; i.e., $C_B = C_T$, but $C_T > C_M$. That situation is depicted by the dashed gray curve in Figure 4. Note however that we specified "at equilibrium." The isochemical repartitioning depends on the kinetics of the carbonate system and thus the hydration/dehydration rates are important. The time scale for molecular diffusion of CO_2 across the equivalent stagnant layer thickness for heat ($\sim$300 μm) should be similar to typical hydration times (i.e., of the order of 100 s). Given the similar time scales and the crudity of the representation of the boundary layers, it is genuinely ambiguous whether equilibrium will be achieved. Note however that below the base of the mass boundary layer, turbulence will be substantial and therefore transport faster than by molecular diffusion
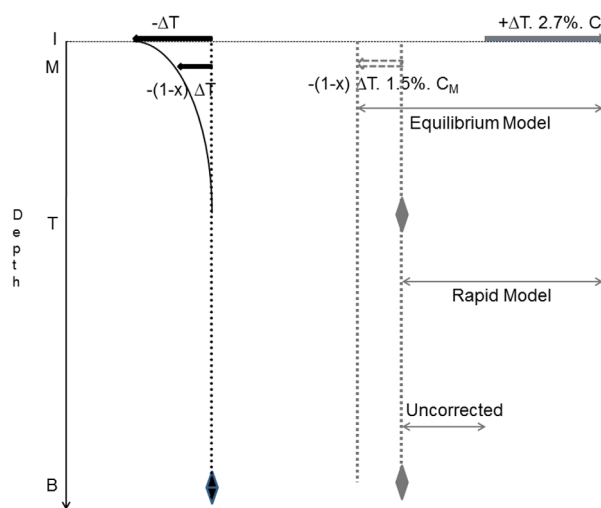
Figure 5. A schematic explaining corrections to concentration difference for the cool skin effect. On the right-hand side of the figure the horizontal gray lines show the calculated span of concentration from the base of the MBL (left-hand arrow head) to the interface (right-hand arrow head). An "uncorrected" concentration difference is calculated using a bulk SST and then corrected using the appropriate temperatures. The main correction is at the interface. In the rapid model that is the only correction, but in the equilibrium model an additional correction is applied at the base of the molecular mass boundary layer. The case of a net downward flux is shown on the left hand side of the figure. Here both corrections increase the concentration difference at the interface and therefore the net downward flux. Where there is a net upward flux apparent from the uncorrected calculation, the concentration difference will be reduced or even reversed by the corrections; thus, the actual net flux will be reduced or reversed.

alone, therefore the diffusion time scale may be significantly shorter than the reaction time scale and there may be insignificant repartitioning of the carbonate species between "M" and "T." The logic of "rapid" diffusion and thus a minimal concentration gradient is shown by the full gray curve in Figure 4. On balance, the "rapid model" is likely to be a better approximation than the "equilibrium model," but there is genuine ambiguity since the models described here are quite crude and the kinetic rates vary. For example, since the time scale of hydration is much less than 100 s in warm seawater, it is possible that the equilibrium model is the better approximation at low latitudes. Note also that it is also possible that some biochemical enhancement of the hydration reaction may occur [*Matthews*, 2000; *Nightingale*, 2009] and these circumstances also favor the equilibrium model.

5. Temperature Mishandling and the Skin Effects

A new analysis of the effect of neglecting the thermal skin effect culminates from the explanations above. Note that "neglecting the thermal skin" most often means using a water temperature measured at depth throughout the calculations of the concentration gradient. As described in section 3, it is sensible to correct CO_2 concentrations to a climatological temperature, ideally for air-sea flux calculations a climatological subskin temperature (SSTsubskin) should be used. A foundation temperature or a "temperature at depth" can be used with the caveat that there may be biases where diurnal warm layers form. However, neither subskin temperature (the temperature at the base of the thermal boundary layer) nor foundation temperature should be confused with the temperatures nearer the sea surface, T_I, T_{Rad}, and T_M described in section 4. Many temperatures are described in the literature as sea surface temperature (SST) including standard products based on the Advanced Very High Resolution Radiometers (AVHRR), but more often these are actually some form of SSTdepth [e.g., *Donlon et al.*, 1999] (note AVHRR Pathfinder data is routinely calibrated to temperatures at depth). As explained in section 4, a true skin radiometric temperature is a useful proxy for either T_I or T_M, while any "bulk" temperature is a good estimate for the temperature at the base of the thermal molecular boundary layer and below if the upper ocean is well mixed. Here we consider the errors incurred by substituting the bulk temperature, T_B, for either or both of T_I and T_M.

As described in section 2, the mechanism for temperature sensitivity differs between the interface and within the main water column. In Figure 5, we show schematically how calculations of concentration that originally ignore the skin effects (i.e., an intake temperature, T_B is used in all calculations) are corrected when the appropriate temperatures are substituted. The interface is sensitive through calculation of the interfacial fugacity (primarily through an error in the estimated vapor pressure) and solubility, with the total effect of an underestimate of the interfacial concentration by typically 2.7% ΔT if T_B is used and the true interfacial temperature is ΔT cooler than T_B. (Note that we use a convention such that ΔT is positive for a cool skin. Beware that compared to the convention adopted in section 2.5, the signs are reversed, i.e., $\Delta T = -dT_I$; while "2.7%" represents a consequent reversal of the sign of "$\Phi_1 + \Phi_2$" in equation (17).) Within the water column including at the base of the MBL, neither of these interfacial effects apply. This is where the analysis of *McGillis and Wanninkhof* [2006] is incorrect. They supposed that overestimating T_M by substituting T_B would lead to a similar (though slightly lower) underestimate of concentration as for the interface,

thus largely counteracting the error in the difference in concentration, but this is a mistake. As described in section 2, the effects of temperature are very different at the interface and within the water column. At the interface, the dry fraction X_{CO_2} is fixed and the effect on concentration operates primarily through solubility and vapor pressure. Within the water column, T_{CO_2} and T_{Alk} should be assumed constant and any sensitivity to temperature is related to repartitioning. As described in section 4 and discussed further below, the response through repartitioning to a temperature gradient between the base of the MBL and the base of the thermal boundary is ambiguous. Overestimating T_M will either have little effect or lead to an overestimate of the concentration at the base of the MBL. The "rapid model" described in section 4 implies that the concentration C_M will not differ significantly from the bulk concentration, C_B, and for this model the basic formula is similar to that used by *Robertson and Watson* [1992] and other early studies, though we prefer to calculate in terms of concentrations rather than fugacity. Thus, according to the rapid model, including the correct skin temperatures where they have been neglected will increase the net invasive flux by increasing the interfacial concentration:

$$dC_I \approx 2.7\% \ \Delta T \ C_I \qquad (23)$$

Any effect of the temperature at the base of the mass boundary layer is related to isochemical repartitioning, which acts in an opposite sense to the effects at the interface and would increase the total effect of including the thermal skin. As explained in section 4, it is unclear whether isochemical repartitioning will occur to a significant extent in this case, but it is worth considering the potential effect. The temperature at the base of the MBL is also unclear, since the MBL resides within the thermal boundary layer. *McGillis and Wanninkhof* [2006] suggested that if the surface was ΔT cooler than T_B, then the base of the MBL would be only perhaps a tenth less cool that is $T_M = T_B - \Delta T \ (1 - 0.1)$. In view of the expected curvature of the temperature profile, one tenth is likely to be an underestimate, but the true fraction, x, is uncertain. We adopt the expression $T_M = T_B - \Delta T \ (1 - x)$ where x is undetermined but probably between 0.1 and 0.5. Thus, according to the equilibrium model, the full equation for the effect of a thermal skin is given by

$$dC \approx 2.7\% \ \Delta T \ C_I + \ 1.5\% \ \Delta T \ (1-x) \ C_M \qquad (24)$$

or more approximately taking $C_I \approx C_M$

$$dC \approx (4.2\% - 1.5\% \ x) \ \Delta T \ C_I \qquad (25)$$

Contrary to the analysis of *McGillis and Wanninkhof* [2006], the fact that the "mass transfer skin" is thinner than the thermal skin can only enhance the importance of the thermal skin, by up to an additional 50% (the maximum is calculated assuming the typical sensitivities of -2.5% and $+1.5\%$ described above, $C_I \approx C_M$, full equilibration and $x \approx 0.1$). However, we think that this is almost certainly an overestimate and given the uncertainties in the calculation of the repartitioning effect it is probably better to focus on the interfacial effect and build the uncertainty into a generous estimate of the uncertainty of ΔT.

Since gas transfer velocities are small at low wind speeds, it is more important to have a reasonably accurate estimate of the thermal skin effect in moderate and high wind speeds. *Donlon et al.* [1999] reported a mean cool skin $\Delta T = 0.14 \ (\pm 0.1)$ K for wind speeds in excess of 6 m/s. Applying the central value of temperature 0.14 K and confidence limits of ± 0.1 K globally with the "rapid model" formula should give a reasonable estimate of the global effect. Thus, a total correction, dC, of the air-sea concentration difference, ΔC, is simply equal to the correction to C_I, given by approximately

$$dC \approx 2.7\% \ \Delta T \ C_I \qquad (26)$$

substituting the simple estimate of the thermal skin deviation, $\Delta T = 0.14 \ (\pm 0.1)$ K, gives

$$dC \approx 0.38 \ (\pm 0.27)\% \ C_I \qquad (27)$$

This formula implies an additional uptake to the oceans of between 0.1 Pg C yr^{-1} and 0.6 Pg C yr^{-1} (with a central estimate of 0.34 Pg C yr^{-1}) on an exchange of ≈ 90 Pg C yr^{-1}, which is substantial compared to an estimate of the contemporary net uptake of 1.6 (± 0.9) Pg C yr^{-1} [*Takahashi et al.*, 2009] that neglects the thermal skin effect. (Note that the calculation above assumes all of the exchange is across the sea surface. The correction should strictly only be applied to direct transfer across the surface (see equations (1) and (2) in section 2), and not to bubble-mediated transfer [*Woolf*, 1993; *Hare et al.*, 2004].)

A more careful calculation using the complete equations for the thermal effects is required, but this simple calculation shows that the thermal skin effect is substantial.

A small additional effect on flux calculations is in the calculation of transfer velocities. Transfer velocities depend on Schmidt number or molecular diffusion coefficient of the dissolved gas, which are temperature dependent. A radiative temperature, T_{rad}, is probably most appropriate to this calculation for transfer directly across the sea surface but T_I is also a reasonable approximation. As shown in sections 2.4–2.6, the error incurred by using an erroneous water temperature in the calculation of transfer velocity can be significant, but the effect is much smaller than the solubility effect for near-saturation conditions.

6. Warm Layers

We have considered the effect of a cool skin and the result of wrongly assigning the relatively warm temperature of underlying water to the top of the skin (the interface, I in Figure 1) and within the thermal skin (the base of the molecular boundary layer, M in Figure 1). There is another opposing case where a relatively cool temperature is wrongly assigned to M and I. This will occur where a nighttime temperature or temperature from a considerable depth is assigned to near the surface during daytime on an occasion where the surface water is significantly warmed forming a layer distinct from the relic mixed layer below (see Figure 3). The formation of warm layers occurs quite commonly during the daytime in low winds and high insolation, commonly referred to as diurnal warming. Where there is some stirring of the surface water, we expect an actively mixing warm layer to form a daytime mixed layer separated by a diurnal thermocline from the relic mixed layer below. For greater insolation and lower winds, the warm layer is relatively intense and shallow. On most days (lower insolation and higher winds), a distinct warm layer will not form though the entire mixed layer may warm very slightly during daytime. Warm layers have been observed and modelled for decades [*Price et al.*, 1986; *Fairall et al.*, 1996]. *McNeil and Merlivat* [1996] pointed out the substantial impact of warm layers on CO_2 fluxes. The improvement of Earth Observation capabilities enabled a more global perspective on warm layers [*Gentemann et al.*, 2003; *Stuart-Menteth et al.*, 2003] and these products have been used to estimate the impacts on CO_2 fluxes [*Olsen et al.*, 2004]. Here we provide only a brief review of the subject.

Similarly to section 5 for the thermal skin, we will consider the effect of wrongly assigning a temperature at depth or nighttime to shallower water. In the case of a warm layer, we will define this warm layer to be ΔT_W warmer than the water in the relic mixed layer and we calculate the effect on CO_2 calculations where the relic or nighttime temperature is incorrectly assigned to the surface water. A thermal skin will be superposed on the warm layer, therefore we assume the interface to be warmer than the relic water by $\Delta T_W - \Delta T$. It is simpler to treat the warm layer effect as a simple additive effect, therefore the specific correction for warm layers will be described below and this should be added to the thermal skin and haline effects.

The effect on the calculated concentrations and fluxes is covered by the theory described in section 2. Thus, the necessary correction to the interfacial concentration if a relic temperature was used initially is given by

$$dC_{IW} \approx -2.7\% \ \Delta T_W C_I \tag{28}$$

Similarly, too low a temperature may be assigned to the base of the MBL and this also needs to be corrected. In this case, unlike the thermal skin, there is no ambiguity that equilibrium repartitioning is appropriate. A warm layer increases the temperature at the base of the molecular boundary, forcing some additional part of the dissolved inorganic carbon into aqueous CO_2. The increase in the concentration at the base of the MBL is then given by

$$dC_{MW} \approx 1.5\% \ \Delta T_W C_M \tag{29}$$

The effect of a warm layer is to decrease the concentration at the interface and increase the concentration at the base of the MBL, in both cases subtracting from the net air-to-sea flux. The total correction, dC_W, of the air-sea concentration difference, ΔC, is given by approximately

$$dC_W \approx -1.5\% \ \Delta T_W C_M - 2.7\% \ \Delta T_W C_I \tag{30}$$

or more approximately taking $C_I \approx C_M$

$$dC_W \approx -4.2\% \ \Delta T_W C_M \approx -4.2\% \ \Delta T_W C_I \tag{31}$$

The warm layer effect is important and will oppose the effect identified for the thermal skin effect. The effect is stronger for a given temperature difference than that associated with the thermal skin effect and the warm layer effect can commonly exceed 2°C [*Gentemann et al.*, 2003] and exceptionally can be much higher [*Merchant et al.*, 2008], thus an order of magnitude greater than the skin effect. On the other hand, warm layers will occur infrequently, typically breakdown at night and predominantly occur in light winds when gas transfer velocities will be low. A detailed and global calculation is beyond the scope of this study, but some indication of the importance of the warm layer is practical by reviewing some previous studies.

McNeil and Merlivat estimated the warm layer effect on the basis of measurements from free floating buoys in the eastern equatorial Pacific and the Mediterranean Sea. For the eastern equatorial Pacific they estimate a daily averaged warming of 0.13°C, almost exactly opposing the typical cool skin effect (0.14°C) [*Donlon et al.*, 1999]. As noted above, the effect of cool skins and warm layers is not equivalent, but this observation does suggest the warm layer effect is of similar importance to the cool skin effect at least in some regions. Much more recently, *Kettle et al.* [2009] have estimated the impact of warm layers in the central Atlantic and Mediterranean Sea using data from the SEVIRI geostationary satellite. The effect is temporally and spatially variable, but *Kettle et al.* [2009] conclude that the effect increases the net flux out of the central Atlantic threefold, though this dramatic result stems from a close balance of influx and outflux in this region. In those publications, the effect on CO_2 flux is calculated by applying a sensitivity of 4.23%/°C to either the water side [*McNeil and Merlivat*, 1996] or the air side [*Kettle et al.*, 2009]; neither of these calculations is strictly correct, but it can be seen from equation (31) that they will be fairly accurate if $C_I \approx C_M$. Taking a broader view of the prevalence and strength of diurnal warming [e.g., *Stuart-Menteth et al.*, 2003], it is apparent that the importance of warm layers will vary enormously from region-to-region. The effect may often be very large (perhaps sufficient to counteract the cool skin effect) in many low latitude regions. The effect will be relatively unimportant in high-latitude regions, but even in the Arctic, diurnal warming events do occur [*Eastwood et al.*, 2011]. The effect of warm layers on CO_2 fluxes globally will be challenging to quantify accurately, but its importance demands attention.

A detailed calculation of warm layer effects requires good input data and a satisfactory model of warm layers. Where concentration is raised by warm layer formation, an outgoing flux is forced, implying a leakage that diminishes the averaged effect [*McNeil and Merlivat*, 1996]. This effect is significant for most gases, but negligible for CO_2 due to the effect of the carbonate system. By a similar argument, it is reasonable to ignore diurnal fluctuations in total CO_2, but it is not satisfactory to ignore the effect of diurnal temperature on the partitioning of the carbonate system. The characteristics of the warm layer and the CO_2 flux depend on detailed meteorological conditions, including cloud coverage and wind speed [*Jeffery et al.*, 2008]. The codependence of warm layer characteristics and gas transfer velocity on wind speed implies that a simple calculation based for example on the diurnal amplitude of the surface temperature and a daily wind speed could be inaccurate, but some simplification will be needed given the limited observational data. *Kettle et al.* [2009] concluded that ignoring the daily structure was acceptable and therefore reasonably accurate calculations were accessible. A more detailed calculation may require the use of one-dimensional models [e.g., *Jeffery et al.*, 2008].

7. Haline Effects

Almost identical considerations to the analysis in sections 2–6 can be applied to haline effects. Effects analogous to those described for temperature (i.e., solubility, vapor pressure, and fugacity effects at the interface, repartitioning effects within the water column) apply to salinity, but the sensitivity of saturated vapor pressure, the fugacity-pressure relationship, solubility, and carbonate speciation each have distinct values for temperature and salinity, all of which follow from the same equations. It is sensible to calculate corrections for salinity at the same time as for temperature since almost identical methods apply and the salinity corrections may also be substantial. Generally, the interface is expected to be more saline than below (thus a "salty skin") due to continual evaporation at the interface. The solubility of aqueous CO_2 reduces with salinity implying that a salty skin reduces interfacial concentration, an opposite effect to a cool skin. The

sensitivity of solubility to salinity according to *Weiss* [1974] is shown in Figure 2d, showing a sensitivity of -0.6% at low sea temperatures diminishing to -0.5% at high sea temperatures.

Zhang and Cai [2007] quote Schmidt numbers, Sc of 7.5, 600, and 780 for heat, CO_2 and NaCl respectively in water at 20°C. To a useful approximation, transfer velocities will scale as $k_i \sim Sc^{-1/2}$ and the equivalent stagnant layer thickness will scale as $L \sim Sc^{-1/2}$. Therefore, in respect of skin effects, the situation for the salty skin is simpler than for the cool skin since the skin layers for gas and salt will be similar in thickness, while the thickness of the thermal boundary layer will be an order of magnitude greater. This implies that there will not be a significant salinity gradient from depth to the base of the MBL and thus no repartitioning effect.

Zhang and Cai [2007] derived a theoretical expression for the salty skin that implies that the salinity difference across the salty skin in practical salinity units is approximately 70% of the negative thermal skin effect in °C. Applying the sensitivities of solubility to salinity and temperature, Zhang and Cai report that the haline and thermal skin effects on CO_2 flux are of very similar magnitude but opposing (each about 0.05 Pg C yr^{-1}). We reject their evaluation of the thermal skin effect and report here our own simple calculations. We adopt the estimate of the cool skin deviation described in section 5, $\Delta T = 0.14$ K and from the simple relationship of Zhang and Cai estimate a salty skin deviation of 70% of 0.14, i.e., $\Delta S \approx 0.1$. Considering the solubility effects alone, the salty skin reduces the downward flux by $\approx 0.6\%$ x $\Delta S \approx 0.06\%$, while the solubility effect of the cool skin increases the downward flux by $\approx 0.35\%$, therefore by this simple formulation the salty skin effect is about one sixth of the thermal effect and opposing. Calculations depend on the magnitude of the salinity anomaly and that is fairly uncertain since the most recent estimates of this anomaly [*Zhang and Zhang*, 2012] are typically a factor of 2.3 greater than a preceding estimate [*Yu*, 2010]. *Zhang and Cai* [2007] included only a solubility effect at the interface and neglected the effect of temperature and salinity on saturated vapor pressure and on the fugacity-pressure relationship. All these effects should be included in a more complete study of the effects of a salty skin.

Corrections within the water column for salinity variations (analogous to those discussed in section 3 for temperature) can be more substantial [*Takahashi et al.*, 2009; *Land et al.*, 2013] and should be included. *Sarmiento and Gruber* [2006] give the salinity dependence of pCO_2 as

$$\partial\, p_{CO_2}/\partial S = \gamma_S p_{CO_2}/S \tag{32}$$

or

$$\partial\, \ln\, p_{CO_2}/\partial\, \ln\, S = \gamma_S \tag{33}$$

where γ_S depends on the specific circumstances. Globally, γ_S has a value of about 1 [*Sarmiento and Gruber*, 2006]; while *Takahashi et al.* [1993, 2009] give $\gamma_S = 0.94$ when the change in salinity results from the admixture of waters with a similar DIC content. Unfortunately, the correction for salinity is quite uncertain since it will vary according to the circumstances of the salinity change. For example, where rainfall is responsible and since rain has a low DIC, the value of γ_S should increase to 1.6 at low latitudes and 1.7 at high latitudes [*Sarmiento and Gruber*, 2006]. $\gamma_S = 1.7$ may also be appropriate for ice melt [*Land et al.*, 2013]. The sensitivity of fugacity to salinity contains both a sensitivity of solubility to salinity (which is subtracted when the change in aqueous concentration is calculated) and the effect of salinity on the carbonate system (which does affect aqueous concentration).

It is clear that calculations of haline effects are worth including but will necessarily be quite uncertain. Some regional modelling of haline effects has been completed [e.g., *Turk et al.*, 2010], but much remains to be done.

8. Discussion of the Major Effects and Implications for Ocean Flux Studies

Two effects are certainly substantial compared to a recent estimate of the contemporary net global sea-to-air flux of carbon dioxide of -1.6 (± 0.9) Pg C yr^{-1} [*Takahashi et al.*, 2009].

First, a bias between the estimated temperature concurrent to the oceanic pCO_2 values and the actual climatological temperature will introduce a bias to the estimated flux of carbon dioxide. Takahashi et al.

included this effect, correcting from the direct estimate of -1.4 (± 0.7) Pg C yr^{-1} to their final estimate of -1.6 Pg C yr^{-1} on the basis of a 0.08 K bias relative to a climatological SST [*Shea et al.*, 1992].

Our study has already motivated a new method of processing temperature and CO_2 data and readers are referred to the resulting methods paper [*Goddijn-Murphy et al.*, 2015] for detail. The basic concept is that shipboard CO_2 measurements should be used in combination with the best gridded temperature data, rather than the estimates of ocean temperature originally paired with the CO_2 measurements. The CO_2 values are transformed from the equilibrator values to that appropriate to the gridded temperature values of the month and location in question, based on an isochemical transformation, as justified in section 3. Therefore, the correction is time and space dependent rather than the simple global bias correction described by *Takahashi et al.* [2009].

Second, the thermal skin effect on carbon dioxide fluxes related to a thermal skin deviation of typically 0.14 K is estimated at ~ -0.34 Pg C yr^{-1} (i.e., implying a greater net flux into the sea). This estimate should be refined based on more detailed calculations.

Of the other thermal and haline effects discussed in this paper, "warm layer effects" are likely to be next in importance and should certainly be revisited. The correct inclusion of warm layers in calculation of carbon dioxide fluxes can be achieved if SSTsubskin or SSTdepth at a reasonably small depth (<1 m) are estimated carefully with due regard for diurnal variation.

9. Conclusions

The air-sea gas flux equation for poorly soluble gases is most unambiguously written in terms of the concentration difference across a thin layer below the air-sea interface. *McGillis and Wanninkhof* [2006] have identified a few important mechanisms by which temperature influences the calculated aqueous concentration gradient of CO_2. We have presented these mechanisms methodically and illustrated with examples that careful handling of temperatures is necessary. The most significant conclusions are summarized below.

We show that neglecting the thermal skin effect and substituting a bulk sea surface temperature in all calculations produces very large errors in the calculated air-sea CO_2 fluxes (in contradiction to *McGillis and Wanninkhof* [2006] but broadly supporting *Robertson and Watson* [1992] and other earlier studies). A cool skin will increase a net downward flux, or decrease a net upward flux. The greater part of the effect results from solubility, vapor pressure, and fugacity calculations at the interface. The solubility and vapor pressure effects are relevant to other poorly soluble gases. Our analysis shows that the difference in characteristic skin thickness between heat and gases can only enhance the importance of skin effects to CO_2 flux calculations. The additional effect arises from repartitioning of the carbonate system during diffusion between the base of the thermal skin and the base of the mass boundary layer (MBL). This effect is ambiguous due to the similar time scales of the diffusion and the hydration-dehydration equilibrium, and is likely to be greatly diminished as a result of the slow hydration reaction. The repartitioning effect has been recognized by *Hare et al.* [2004], but we have written the effect in terms of concentrations for greater clarity.

Effects at the interface and the base of the MBL are associated with warm layers; in this case, there is no ambiguity in the effect of repartitioning, which will have a strong effect. A warm layer will reduce the interfacial concentration and increase the subskin concentration, the two sets of effect reinforce each other to increase net upward flux or decrease downward flux.

All calculations of aqueous concentration within the water column require consistency in temperature values and should use the best possible values. Correction of CO_2 values is necessary where the temperature is corrected. That correction usually must be based on an isochemical transformation, implying repartition of the carbonate species. For example, shipboard fugacity measurements should be corrected, both to correct for warming prior to measurement and to correct for sampling anomalies in temperature and salinity. An assumption of "constant chemistry" can never be wholly satisfactory, but for temperature effects it is usually the best option. Transformations between different seasons should be avoided since seasonal changes are unlikely to be isochemical in nature.

Corrections for salinity variations are more difficult. It is necessary to consider both thermal and haline effects in any thorough analysis of air-sea gas fluxes, but the thermal effects are more substantial.

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