Analytical Uncertainties of Surface Water pCO_2: A Potential Bias in Estimates of Oceanic Carbon Uptake

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Abstract

The analytical uncertainties in the CO_2 fugacity (fCO_2) of surface sea water are investigated using a chemistry model of the carbonate system and Gaussian error propagation. We find a typical 2-σ uncertainty in fCO_2 of 1% if the fugacity is determined by mole fraction measurements on air equilibrated with the sample at or close to in-situ temperature. Frequently, equilibrated air is analyzed at a constant temperature of 25, 20, or 4 °C and it proves necessary to correct for differences between in-situ temperature and the temperature of the equilibrated air. A comparison between our full chemistry calculation and an exponential temperature correction method [*Takahashi et al.*, 1993] shows systematic deviations as large as 30 μatm when correcting for temperature differences up to 20 °C as exploited for Antarctic samples [*Chipman et al.*, 1994]. The exponential correction always yields larger fCO_2 at in-situ temperature if the mole fraction measurements were done at 20 °C. Deviations are largest for high-latitude samples. Our results imply (1) that published estimates of the air-sea partial pressure difference could be seriously biased depending on the temperature correction method applied; (2) that published estimates of global air-sea net carbon fluxes [*Tans et al.*, 1990; *Takahashi et al.*, 1997] may be too low by as much as a GtC yr^{-1}; (3) or ,alternatively, that published chemical equilibrium constants may not be adequate for seawater.

Key Words: CO_2, fugacity, analytical methods, carbonate chemistry

1 Introduction

The oceans are one of the major sinks for anthropogenic carbon released into the atmosphere. Based on observation of CO_2 partial pressure, the (local) net air-to-sea flux, F, of carbon dioxide can be calculated from a relation of the form

$$F = k_g \Delta f\mathrm{CO}_2 \ , \tag{1.1}$$

where k_g is the gas-phase related transfer coefficient which depends sensitively on wind speed and related quantities (e.g. [*Liss and Merlivat*, 1986; *Heimann and Monfray*, 1989; *Etcheto et al.*, 1991; *Wanninkhof*, 1992; *Schudlich and Emerson*, 1996]). $\Delta f\mathrm{CO}_2$ is the difference between the fugacity of CO_2 in water and air, which acts as the driving force for a net air-sea flux of CO_2. The fugacity accounts for the non-ideal behavior of CO_2 gas. fCO_2 of sea water is about 0.3 to 0.4 permil lower than the corresponding partial pressure of an ideal gas [*Weiss*, 1974]. Typically, values for $\Delta f\mathrm{CO}_2$ are in the range 0 to $\pm$ 30 μatm, with a global mean of a few μatm, i.e. only 2-3 % of the absolute value of fCO_2. Therefore, it is essential that $\Delta f\mathrm{CO}_2$ is calculated accurately, otherwise computed fluxes may be seriously wrong.

Major efforts (e.g. [*Merlivat and Vézina*, 1992; *Sabine et al.*, 1997]) are required in order to collect data on the CO_2 partial pressure, pCO_2, of the surface ocean. Using the data from such efforts, *Takahashi et al.* [1997] have compiled a global map of surface water pCO_2. Maps of surface ocean pCO2 and of implied air-sea carbon net fluxes are used (1) to estimate the net air-to-sea carbon flux and thus oceanic storage of anthropogenic carbon [*Tans et al.*, 1990; *Sarmiento and Sundquist*, 1992; *Takahashi et al.*, 1997]; (2) as a data constraint in inverse modeling studies where regional carbon sources and sinks are deduced from observations of the spatial distribution of atmospheric CO_2 concentration in combination with an atmospheric transport model [*Tans et al.*, 1990; *Enting et al.*, 1995; *Denning et al.*, 1997]; and (3) to validate ocean models used to simulate the marine carbon cycle and anthropogenic CO_2 uptake [*Sarmiento et al.*, 1995; *Murnane et al.*, 1997]

There is a long list of problems associated with estimating sea surface fCO_2 from local measurements and for global compilations. These problems include the extrapolation of observations taken at shallow depths to the surface, extrapolation of relatively sparse measurements to regional scales, the covariance between gas transfer coefficient and partial pressure difference, and uncertainties in the gas transfer coefficient (e.g. [*Van Scoy et al.*, 1995]). There are additional difficulties associated with the experimental procedure used to determine fCO_2.

Here, we wish to consider in more detail the precision of fCO_2 calculated by two different methods and the effect of temperature corrections for fCO_2 measurements made at temperatures that differ from the sea surface temperature. The first method, $\mathcal{M}_{DIC}$, calculates fCO_2 using measurements of T, S, DIC, and TA and equilibrium constants (e.g. [*Keeling*, 1993; *Winn et al.*, 1994; *Bates et al.*, 1996]). In the second method, $\mathcal{M}_{xCO_2}$, measurements are made of the mole fraction of CO_2 in air equilibrated with a seawater sample at an equilibrator temperature, $\widehat{T}$ (see e.g. [*Körtzinger et al.*, 1996] and references therein) and a temperature correction is applied to determine the in-situ fCO_2.

In many cases where fCO_2 is determined via $\mathcal{M}_{xCO_2}$ measurements have been made at a fixed equilibrator temperature ($\widehat{T}$) of 20, 4 °C (e.g. [*Chipman et al.*, 1993; *Chipman et al.*, 1994; *Chipman et al.*, 1997; *Smethie et al.*, 1985; *Takahashi et al.*, 1991; *Takahashi et al.*, 1993; *Takahashi et al.*, 1995; *Takahashi et al.*, 1996]) or 25 °C [*Andrié et al.*, 1986; *Copin-Montégut and Avril*, 1995; *Oudot et al.*, 1995] and a temperature correction is applied to determine the CO_2 fugacity at in-situ temperature, T_s. To avoid significant errors this correction has to be accurate to about 1 permil. In other cases continuous flow equilibrators measure the mole fraction at close to in-situ temperature. Temperature differences between equilibrated air and seawater typically vary between 0.1 and 1 °C (e.g. [*Inoue and Sugimura*, 1995; *Ishii and Inoue*, 1995; *Landrum et al.*, 1996; *Metzl et al.*, 1995; *Murphy et al.*, 1995; *Poisson et al.*, 1993; *Robertson et al.*, 1993; *Schneider and Morland*, 1995; *Watson et al.*, 1991; *Weiss et al.*, 1992; *Wong and Chan*, 1991; *Wong et al.*, 1995]).

We present two approaches for correcting fCO_2 to in-situ temperatures with the $\mathcal{M}_{xCO_2}$ method. Our primary method (the chemistry model) of correcting for differences between in-situ seawater and equilibrator temperature uses chemical equilibria [*Dickson*, 1990; *Millero*, 1995; *Weiss*, 1974] and procedures based on recommendations by [*UNESCO*, 1987]. The other approach uses an exponential relationship between temperature and fCO_2 developed by Takahashi and co-workers using results of measurements on seawater samples [*Takahashi et al.*, 1993]:

$$f\mathrm{CO}_{2water}(T_s) = f\mathrm{CO}_{2water}(\widehat{T})\ exp(0.0423[T_s - \widehat{T}]. \tag{1.2}$$

This exponential correction has been applied to samples from water masses which cover the range of temperatures (-1.6 to 28 °C), salinity, and chemical composition found in the surface ocean.

Other equations have been derived from results of chemical equilibrium models to determine pCO_2 at different temperatures when only T, S and pCO_2 are known [*Gordon and Jones*, 1973; *Weiss et al.*, 1982; *Copin-Montégut*, 1988; *Copin-Montégut*, 1989; *Goyet et al.*, 1993; *Millero*, 1995]. These formulations are not explicitly investigated here but are closely related to our chemistry model approach.

If the exponential temperature correction (Equation 1.2) and the chemical equilibria approach are consistent, then the corrected in-situ fCO_2 should be consistent. However, we find the two corrections can produce systematic differences of up to 30 μatm. This discrepancy implies that published maps of the air-sea fCO_2 difference and estimated net carbon fluxes, such as those produced by *Tans et al.* [1990] and *Takahashi et al.* [1997], could be strongly biased depending which temperature correction was used to calculate the in-situ fCO_2. On the other hand, if the empirical data based relationship of *Takahashi et al.* [1993] is close to reality, then published chemical equilibrium constants (e.g. [*Goyet and Poisson*, 1989; *Millero*, 1995; *Roy et al.*, 1993]) as used in our chemistry model must be questioned.

A variety of issues related to the accuracy and precision of surface seawater fCO_2 and carbon system parameters have been discussed before [*Copin-Montégut*, 1988; *Dickson and Riley*, 1978; *Dickson and Goyet*, 1994; *Goyet et al.*, 1993; *Lee and Millero*, 1995; *Millero et al.*, 1993]. Our contribution is to present a complete analysis of the uncertainties in fCO_2 due to commonly measured terms such as T and S, as well as nutrients, borate, and the other carbon system parameters. We use Gaussian error propagation to calculate the overall uncertainty in fCO_2 due to errors in all the parameters used in the calculation. We now describe how fCO_2 is calculated using $\mathcal{M}_{DIC}$ or $\mathcal{M}_{xCO_2}$ and define artificial seawater samples before analyzing errors in fCO_2 that are associated with uncertainties in equilibrium constants and other measured or derived parameters. We then compare results of the temperature correction obtained with the chemistry model and the exponential approach. In the appendix, we document the chemistry model that was used for the present analysis and that is implemented in models of the marine carbon cycles at Bern and Princeton.

2 Methods

$\mathcal{M}_{DIC}$:

In the approach called $\mathcal{M}_{DIC}$ (e.g. [*Keeling*, 1993; *Winn et al.*, 1994; *Bates et al.*, 1996]), the fugacity of a sample was computed from the measured concentrations of total dissolved inorganic carbon (TCO_2), total alkalinity (TA), total phosphate (TP), and total silicate (TSi), as well as from temperature (T) and salinity (S). A linear relationship was used to estimate total borate (TB) from salinity [*Uppström*, 1974]. The dissolved species of TSi, TP, and TB form various acid-base pairs which contribute to the total alkalinity and thus to the chemical buffering of the system. The eight equilibrium constants considered are summarized in Tab. 1. The exact procedure to compute the fugacity and the definitions of TCO_2, TA, TB, TP, and TSi are outlined in detail in Appendix A.

A Gaussian error propagation was performed to calculate overall uncertainties in fCO_2 using the chemistry model and the specified uncertainties in the 5 concentrations, C, and the 8 required equilibrium constants as well as in the sea water temperature, T_s, and salinity, S, measurements(Tab. 1). The uncertainties in the equilibrium constants due to errors in temperature and salinity measurements were also considered in the error propagation calculation. TB was computed as a function of salinity whereas the other concentrations are measured and thus independent of temperature and salinity. The following equation was evaluated numerically using the chemistry model to obtain the overall error in the fugacity, ΔfCO_2 :

$$
\begin{aligned}
(\Delta fCO_2)^2 = & \sum_{C_i \in \mathcal{C}} \left(\frac{\partial fCO_2}{\partial C_i} \cdot \Delta C_i \right)^2 \\
& + \sum_{K_i \in \mathcal{K}} \left(\frac{\partial fCO_2}{\partial K_i} \cdot \Delta K_i \right)^2 \\
& + \sum_{K_i \in \mathcal{K}} \left(\frac{\partial fCO_2}{\partial K_i} \frac{\partial K_i}{\partial T_s} \cdot \Delta T_s \right)^2 \\
& + \sum_{K_i \in \mathcal{K}} \left(\frac{\partial fCO_2}{\partial K_i} \frac{\partial K_i}{\partial S} \cdot \Delta S \right)^2 + \left(\frac{\partial fCO_2}{\partial TB} \frac{dTB}{dS} \cdot \Delta S \right)^2
\end{aligned}
\tag{2.3}
$$

The first sum of the right hand side accounts for the errors due to uncertainties in the measurements of TA, TCO_2, TSi, TP and the error in the TB - S relationship; the second accounts for errors due to uncertainties in the equilibrium constants; the third terms accounts for errors due uncertainty in temperature; the last two term accounts for errors due to uncertainty in measured salinity. The sets $\mathcal{K}$ and $\mathcal{C}$ include the 8 equilibrium constants (see Tab. 1) and the 5 concentrations (TCO_2, TA, TP, TB, TSi) respectively. We have neglected the effect of atmospheric pressure variations (± 30 hPa) on fCO_2 which are negligible.

The results of the error propagation are sensitive to the assumed uncertainties in concentrations, equilibrium constants, and sea surface temperature and salinity (Tab. 1). Large 2-σ errors relative to instrument precision were adopted for sea surface temperature and salinity in an attempt to include uncertainties arising from micro scale variations in the water column, instrument inertia and drift, and ship of opportunity sampling conditions. Estimating total uncertainties for the carbonic acid dissociation constants evaluated at a given temperature and salinity is difficult. Published uncertainties for the dissociation constants of carbonic acid vary by up to a factor of five (Tab. 2). Furthermore, these estimates are based on how well the data points can be predicted with an analytical expression. This uncertainty differs from the total uncertainty which is needed for the error propagation calculation. We used the uncertainties published by *Millero* [1995] for the data of *Roy et al.* [1993], thereby adapting mid range estimates.

$\mathcal{M}_{xCO_2}$:

The fugacity of CO_2 in seawater can be estimated from the measured mole fraction of dried air, xCO_2, equilibrated with the sea water sample (method $\mathcal{M}_{xCO_2}$) according to:

$$\widehat{fCO_2} = K_f(\widehat{T}, P_{atm}) \cdot \Big(P_{atm} - e_w(\widehat{T}, S)\Big) \cdot xCO_2 \tag{2.4}$$

The symbol $\hat{}$ refers to the temperature at which the mole fraction is measured in the equilibrator. K_f is the fugacity coefficient which accounts for non-ideal behavior of CO_2. K_f is a function of measured atmospheric pressure, P_{atm}, and equilibrator temperature, $\widehat{T}$, [*Weiss*, 1974]. The vapor pressure of air above sea water, e_w, was calculated as a function of temperature and salinity, S, [*Weiss and Price*, 1980]. For practical reasons, xCO_2 in discrete samples is often measured at constant temperature of e.g. 25, 20, or 4 °C. Thus, the temperature of the analyzed air ($\widehat{T}$) is usually different from the in-situ temperature of the sea water sample (T_s). This requires a temperature correction to determine the in-situ fugacity at T_s. The largest differences between $\widehat{T}$ and T_s are usually observed for cold sea temperatures and may be as large as 22 K for Arctic and Antarctic waters. On the other hand, continuous flow equilibrators measure xCO_2 at close to in-situ temperature. Temperature differences between equilibrated air and seawater typically vary between 0.1 and 1 °C.

The TCO_2, TA, TP, TSi, and the chemistry model (method $\mathcal{M}_{DIC}$, Appendix A) was used to compute the change in fCO_2 due to the temperature correction. Thus, the correction term, δfCO_2, was obtained as difference between the fugacities calculated (as in method $\mathcal{M}_{DIC}$) at $\widehat{T}$ and T_s.

$$\delta fCO_2 = fCO_2(\mathcal{C}, \mathcal{K}(T_s, S)) - fCO_2(\mathcal{C}, \mathcal{K}(\widehat{T}, S)) \tag{2.5}$$

The uncertainty of the fugacity based on $\mathcal{M}_{xCO_2}$ at T_s was calculated using Gaussian error propagation and the estimated overall uncertainties of K_f, P_{atm}, e_w, and xCO_2 as given in Tab. 1. The additional uncertainty due to the temperature correction was included through error propagation on the terms in Eq. 2.4. Details are given in Appendix B.

Definition of artificial seawater samples:

Cold and Warm Sample: It is assumed that TCO_2, TA, TSi, TP, salinity and temperature are known for method $\mathcal{M}_{DIC}$. In addition, xCO_2 and P_{atm} are assumed to be known for method $\mathcal{M}_{xCO_2}$. We define two artificial samples to investigate uncertainties in the fugacity determination for the two methods $\mathcal{M}_{DIC}$ and $\mathcal{M}_{xCO_2}$ (Tab. 3). The two samples represent typical surface water from low- (Warm Sample) and high- (Cold Sample) latitudes. The mole fraction of the samples required to evaluate method $\mathcal{M}_{xCO_2}$ is calculated with the chemistry model and thus consistent with the prescribed concentrations.

5-degree Samples: Zonal average surface values were calculated for the Atlantic, Pacific and Indian Ocean and for 5 degree latitude belts. This larger data set was used to check the findings based on Cold and Warm Sample. Averaged concentrations for TCO_2, TA, TSi, were calculated using the GEOSECS and TTO data. Temperature, salinity and phosphate values are obtained by averaging the Levitus data [*NOAA*, 1994]. Fugacities and mole fraction were calculated with the chemistry model for each 5-degree Sample at different temperatures (SST, 4 and 20 °C) by applying the chemistry model. Fugacities of this artificial data set vary between 150 and 500 μatm at 'in-situ' temperature.

3 Results

We now examine the sources of errors in fCO_2 predicted using $\mathcal{M}_{DIC}$ and $\mathcal{M}_{xCO_2}$. Individual and overall uncertainties are dependent on the assumed uncertainties in individual parameters, we use the values in Table 1 for the purposes of our calculations. The actual errors in fCO_2 will vary with sampling and analytical conditions.

We first investigate errors in fCO_2 estimated with $\mathcal{M}_{DIC}$ over a range of T_s. Uncertainties due to equilibrium constants and concentration measurements are about the same order of magnitude and vary between 3 and 13 μatm (Fig. 1). Individual contributions to uncertainties in fCO_2 larger than 3 μatm were found for the first and second dissociation constant of carbonic acid, and for TA, TB, and TCO_2 (Fig. 2). The uncertainty in SST leads to an error in fCO_2 of 2 to 4 μatm; uncertainty in the salinity measurement translates into an error of about 1 μatm. For the Cold Sample, the uncertainty in alkalinity plays the dominant role. Uncertainty in the TB - S relationship (3-8 μatm) causes errors in TB to be the largest source of uncertainty in the Warm

Sample. This error could be reduced substantially if TB is measured precisely instead of calculated from measured salinity. The combined 2-σ uncertainty due to the dissociation constants for water, silicic acid, and phosphoric acid are less than 0.5 μatm because the contribution of [OH^-], [H^+], [HPO_4^{2-}], [PO_4^{3-}], [H_3PO_4], and [$Si(OH)_3O^-$] to total alkalinity are small. Uncertainties from errors in the total silicate and phosphate concentration are negligible (not plotted). Concentrations of TA, TCO_2, TB and the two dissociation constants of carbonic acid must be known more precisely to significantly reduce errors in fCO_2 calculated with $\mathcal{M}_{DIC}$.

Next, the contribution of individual parameters to the overall uncertainties in fCO_2 for the mole fraction measurements (method $\mathcal{M}_{xCO_2}$) are investigated. The temperature correction for differences between equilibrator and in-situ temperature are based on the chemistry model (Appendix A). We found that the errors due to inaccuracies in SST were 95-98 % of the overall uncertainties (as obtained by quadratic error addition) for the Cold and Warm Sample when assuming a 2-σ error in SST of 0.2 °C and SST equal $\widehat{T}$. Uncertainties due the the other variables are smaller than 0.9 μatm. Thus, fCO_2 predicted using $\mathcal{M}_{xCO_2}$ at temperature close to T_s is quite precise (within $\approx$ 3 μatm).

Uncertainties due to the correction between in-situ temperature of the sample and equilibrator temperature can be substantial if there is a large temperature difference. In Fig. 3 the uncertainties in fCO_2 as obtained by analyzing the sample at 20 °C (e.g. [*Chipman et al.*, 1993; *Chipman et al.*, 1994; *Smethie et al.*, 1985; *Takahashi et al.*, 1991; *Takahashi et al.*, 1993; *Takahashi et al.*, 1995; *Takahashi et al.*, 1996], 4 °C [*Chipman et al.*, 1997], and in situ temperature are plotted versus the in-situ temperature. Uncertainties in fCO_2 increase rapidly with increasing difference between $\widehat{T}$ and SST and can in extreme cases be as large as 20 μatm. Therefore, fCO_2 should be measured with $\widehat{T}$ as close to T_s as possible.

Differences in equilibrator and in-situ temperature vary typically between 0 and 1 °C for continuous flow equilibrators. We found that the uncertainty arising from the temperature correction alone is smaller than 0.1 μatm for temperature difference smaller than 1 °C, and smaller than 1 μatm for temperature differences smaller than 3 °C for the 2 artificial samples at 4 and 20 °C, respectively. An analysis of the uncertainties due to the temperature correction (Fig. 4; see Appendix B for details) shows that the concentrations of TA, TB, TCO_2, and the two dissociation constants of carbonic acid must be known substantially better to reduce the 2-σ uncertainty in the temperature correction term that is based on the chemistry model.

Alternative methods of correcting for differences between equilibrator and in-situ temperatures such as (Equation 1.2) could be more precise than the corrections based on the chemistry model. [*Takahashi et al.*, 1993] exploit an exponential dependency of fCO_2 on temperature between a temperature range of 2 to 28 ^{o}C and a salinity range of 34 to 36. This relationship has also been used for temperatures as low as -1.7 °C [*Chipman et al.*, 1997]. It has the advantage that the concentrations of TCO_2, TA, TP, and TSi are not required.

We compared the fCO_2 of the 5-degree Samples predicted using the two temperature correction techniques and found systematic deviations between the two corrections (Fig. 5). For an equilibrator temperature of 20 °C, the exponential correction yields higher fCO_2 values than those obtained with the chemistry model. Deviations are larger than 5 μatm if the in-situ and equilibrator temperature difference exceeds 8 °C. For an equilibrator temperature of 4 °C, differences between the two methods exceed 5 μatm when correcting for temperature differences of more than 2 °C. Such differences are larger than the estimated uncertainty for the chemistry model correction. Using only this information it is not possible to determine which correction method is more appropriate; but, it seems clear that the difference between $\widehat{T}$ and T_s should be kept small.

In Fig. 6 the 2-σ uncertainties of fCO_2 determined with $\mathcal{M}_{xCO_2}$ and $\mathcal{M}_{DIC}$ are plotted versus sample temperature. For method $\mathcal{M}_{xCO_2}$the optimal case occurs when the temperature of the analyzed air is set equal to the in-situ temperature of the sample and no temperature correction is required. In this case uncertainties vary between 3.4 and 4.3 μatm for the Cold Sample and between 1.9 and 3.9 μatm for the Warm Sample. For method $\mathcal{M}_{DIC}$, uncertainties are substantially larger and range up to 16 μatm. Thus, the overall uncertainties in fCO_2 determined via the chemistry method ($\mathcal{M}_{DIC}$) are of the same order or larger than basin wide air-sea fCO_2 differences.

Errors in fCO_2 were also calculated for the 5-degree Samples (see Methods section). We found no significant difference between fCO_2 uncertainties calculated for this data and those calculated for the Cold and Warm Sample. The relative errors in fCO_2 are a smooth function of temperature (Fig. 7). Uncertainties in fCO_2 are around 1% for mole fraction measurements at in-situ temperature and between 3 and 4% when applying method $\mathcal{M}_{DIC}$.

4 Discussion and Conclusions

When fCO_2 was calculated from measured concentrations using $\mathcal{M}_{DIC}$ the relative 2-σ uncertainties are on the order of 3-4 % (10-14 μatm for fCO_2= 350 μatm). These error calculations compare well with earlier work [*Lee and Millero*, 1995; *Millero et al.*, 1993] in which fCO_2 measurements are within $\pm$ 12-18 μatm (2-σ) of fCO_2 predicted from concentration measurements and thermodynamic constants of *Goyet and Poisson* [1989] and *Roy et al.* [1993]. We found that contributions to the overall fCO_2 uncertainty from TA, TCO_2, and TB and the first and second dissociation constants of carbonic acid contribute are on the same order. Thus, errors in a variety of parameters need to be reduced to improve the precision of fCO_2 calculated using $\mathcal{M}_{DIC}$. Perhaps the easiest way to reduce fCO_2 errors would be to directly measure TB instead of deriving TB from the linear relationship between salinity and TB.

The most precise estimate of fCO_2 was calculated using $\mathcal{M}_{xCO_2}$ when the equilibrator temperature equaled the in-situ temperature. The relatve 2-σ error in fCO_2 is then close to 1 % (3.5 μatm for fCO_2= 350 μatm) assuming a 2-σ uncertainty in seawater temperature of 0.2 °C. Apparently it is difficult in practice to keep the equilibrator temperature equal to in-situ temperature. Published temperature differences between bulk sea water and continuous flow equilibrators vary typically between 0.1 and 1 °C. This temperature variation is not a significant problem as the uncertainty due to the temperature correction alone was found to be of order 0.1 μatm for a temperature difference of 1 °C.

In other cases, temperature differences can be as large as 20 °C (e.g. [*Chipman et al.*, 1994]) and the temperature correction amounts to more than several hundred μatm. This correction is of the same order as the fCO_2 signal and an order of magnitude larger than the air-sea fCO_2 difference. Large differences between equilibrator and in-situ temperatures produce 2-σ uncertainties up to 20 μatm when the chemistry model (Appendix A) is used to make temperature corrections. A significant fraction (up to 15 μatm) of this uncertainty stems from the first and second dissociation constants for carbonic acid. As *Goyet and Poisson* [1989] suggest, it is best to minimize the difference between measured and in-situ temperature. For a temperature correction of up to 10 °C from a measurement temperature of 20 °C, *Goyet and Poisson* [1989] use a polynomial to fit within 5 μatm fCO_2 predicted with their chemistry model. This 1-σ uncertainty is on the same order as the analytical uncertainty we found due to the temperature correction.

If the exponential temperature correction (Equation 1.2) and the chemical model correction are consistent, then in-situ fCO_2 estimates based on the two approaches should agree. However, we find the two corrections can produce systematic differences of up to 30 μatm. For an equilibrator temperature of 20 °C (e.g. [*Chipman et al.*, 1993; *Chipman et al.*, 1994; *Smethie et al.*, 1985; *Takahashi et al.*, 1991; *Takahashi et al.*, 1993; *Takahashi et al.*, 1995; *Takahashi et al.*, 1996]) fCO_2 at in-situ temperature is always larger if the exponential method is used. For an equilibrator temperature of

4 °C (e.g. [*Chipman et al.*, 1997]), the deviation between the two method follows a linear trend of about 2.5 μatm°C^{-1}; the exponential method yields larger fCO_2 when in-situ temperature is less than 4 °C.

There are several possible causes for the systematic differences in temperature corrections. Among them are: 1) Takahashi and his co-workers [*Takahashi et al.*, 1993] use the *Mehrbach et al.* [1973] carbon equilibrium constants, and 2) most equilibrium constants are determined in artificial seawater whereas *Takahashi et al.* [1993] used seawater to construct their exponential relationship.

Uncertainties in fCO_2 have broad implications for studies of the global and ocean carbon cycles:

(1) If the exponential method is correct, then published equilibrium constants and their temperature dependency (e.g. [*Goyet and Poisson*, 1989; *Millero*, 1995; *Roy et al.*, 1993]) must be questioned. This would affect studies which calculate fCO_2 from measurements of TCO_2, TA, and other carbonate chemistry parameters for various purposes such as for consistency checks of mole fraction measurements or carbon budget analyses. However, we do not expect that eventual revisions in the equilibrium constants and their temperature dependency would seriously affect prediction of anthropogenic CO_2 uptake obtained by ocean transport models. We find that the increase in pCO_2 divided by the increase in DIC (ΔpCO_2 / $\Delta\Sigma CO_2$) of surface water is within a range of 13% at 0 °C, 8% at 10 °C, and of 5% at 20 °C and 30°C when emplyoing 6 different sets of equilibrium constants [*Buch*, 1951; *Edmond and Gieskes*, 1970; *Goyet and Poisson*, 1989; *Hansson*, 1973; *Lyman*, 1956; *Mehrbach et al.*, 1973] at a CO_2 partial pressure of 280 and 400 ppm.

(2) *Wanninkhof and Feely* [1996] suggest that fCO_2 measured at 20 °C ($fCO_2(20)$) is a powerful tracer of physical transport and biological transformation in sub-surface water. Unfortunately, conversion to $fCO_2(20)$ from fCO_2 at in-situ temperature and vice versa can potentially introduce large and systematic errors. Thus, temperature correction methods need to be refined in order to fully exploit the information of the numerous measurements of $fCO_2(20)$ and fCO_2 at $\approx T_s$.

(3) Published maps of the air-sea fCO_2 difference, such as those produced by *Tans et al.* [1990] and *Takahashi et al.* [1997], could be strongly biased depending on which temperature correction was used to calculate the in-situ fCO_2. Potential biases are largest in the high-latitude oceans.

(4) If the chemistry model and related uncertainties are correct, then the global net air-to-sea carbon fluxes as estimated using fCO_2 data analyzed at 20 °C and corrected by the exponential approach may be considerably too low. An average analytical uncertainty in fCO_2 of 4 μatm translates into a global net air-sea flux uncertainty of 1 GtC yr^{-1} with using an effective air-sea gas exchange coefficient of 0.07 mol CO_2 m^{-2} year^{-1} μatm^{-1} [*Broecker et al.*, 1985]. This number ignores correlations between gas transfer velocities and ΔfCO_2, but it illustrates the effect of analytical uncertainty in fCO_2 on air-sea gas fluxes.

(5) Atmospheric modeling studies that make use of surface ocean

fCO_2 data as a constraint may yield biased results for the distribution of oceanic and terrestrial carbon sources and sinks.

As both the exponential correction and chemical equilibrium constants are based on measurements, we are not in a position to decide which method is closer to reality. However, it appears clear that the discrepancy between the two method must be resolved to increase our confidence in surface ocean fCO_2 data and deduced results.

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A Seawater carbon chemistry model

In the following section a chemistry model is described which was used for the error calculations and which is also implemented in models of the marine carbon cycle at the Universities of Bern and Princeton. All equations and numerical values used in the model are taken from the literature. As we found it cumbersome for a non-specialist to build correctly such a chemistry module based on published literature, we summarize our efforts for other modelers below. We will first describe units and pH scales used in the model, then give formal definitions of total concentrations and chemical equilibria, summarize the numerical description of equilibrium constants as a function of temperature and salinity, and turn finally to the calculations of the concentrations of individual carbon species and the fugacity using measurements of total dissolved inorganic carbon, alkalinity, and related concentrations.

Units and pH-scales: It is important that all dissociation constant used in chemical calculations are related to the same pH scale and concentration units. We use as a standard the sea-water scale and units of mol per kg of solution [*Dickson*, 1984].

The symbol "(X)" is used for molality, i. e. mol per kg of *solvent* (H_2O), and "[X] " for mol per kg of *solution* (sea water) to express the concentration of a chemical species X. The two units are related by (c. f. [*Millero*, 1995]):

$$[X] \quad = \quad \left(1 \,-\, 1.005 \cdot 10^{-3}\, S\right) \cdot (X) \tag{A.1}$$

S is the salinity. The product $1.005 \cdot S$ yields grams of sea salt per kg of seawater.

In the description of weak acid equilibria various types of pH scales such as the N.B.S. scale, the 'free' hydrogen ion concentration scale, the total hydrogen ion concentration scale or sea-water scale (SWS) have been used c. f. [*UNESCO*, 1987], [*Dickson*, 1984]. SWS is a special case of the total hydrogen ion concentration scale including HF (e. g. see [*Roy et al.*, 1993]). The appropriate pH scale should be used for a given set of equilibria constants.

In pH(SWS) scale, the total concentrations can be written following the expressions as given in [*Goyet and Poisson*, 1989], thereby including in the definition of total H^+, OH^-, HCO_3^-, and CO_3^{2-} concentrations the formation of complexes with Na, Mg, Ca, K, and Sr ions. The total hydrogen ion concentration includes also the formation of HSO_4^- and HF. The CO_2 concentration is defined as the sum of dissolved CO_2 plus the H_2CO_3 molecules, which contributes a fraction (10^{-3}) to the total CO_2 concentration [*Millero*, 1995] for the typical pH of the ocean.

Total concentrations and alkalinity: It is convenient to define total dissolved inorganic carbon, TCO_2, total borate, TB, total phosphate, TP, total silicate, TSi and total alkalinity, TA:

$$TCO_2 \quad = \quad [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{A.2}$$

$$
\begin{aligned}
TB &= [\mathrm{B(OH)_3}] + [\mathrm{B(OH)_4^-}] && \text{(A.3)}\\
TP &= [\mathrm{H_3PO_4}] + [\mathrm{H_2PO_4^-}] + [\mathrm{HPO_4^{2-}}] + [\mathrm{PO_4^{3-}}] && \text{(A.4)}\\
TSi &= [\mathrm{Si(OH)_4}] + [\mathrm{Si(OH)_3O^-}] && \text{(A.5)}
\end{aligned}
$$

The definition of total alkalinity related to the pH(SWS) scale is given by (see e. g. [*UNESCO*, 1987]):

$$
\begin{aligned}
TA &= A_c + A_b + A_{Si} + A_P + A_w && \text{(A.6)}\\
A_c &:= [\mathrm{HCO_3^-}] + 2\,[\mathrm{CO_3^{2-}}] && \text{(A.7)}\\
A_b &:= [\mathrm{B(OH)_4^-}] && \text{(A.8)}\\
A_{Si} &:= [\mathrm{Si(OH)_3O^-}] && \text{(A.9)}\\
A_P &:= [\mathrm{HPO_4^{2-}}] + 2\,[\mathrm{PO_4^{3-}}] - [\mathrm{H_3PO_4}] && \text{(A.10)}\\
A_w &:= [\mathrm{OH^-}] - [\mathrm{H^+}]
\end{aligned}
$$

A_c, A_b, A_{Si}, A_P, and A_w, are the carbonate, borate, silicate, phosphate and water alkalinity. It should be noted that the zero level of protons for the phosphoric acid is related to $H_2PO_4^-$. Therefore the weight of PO_4^{3-} is 2, and for H_3PO_4 it is -1. For details see [*Dickson*, 1981].

Carbonate alkalinity comprises the largest fraction of TA but the contribution due to borate should not be neglected, if accurate CO_2 values are needed. Here, we also take into account the effect of self dissociation of water, total phosphate, and silicate, which influence the CO_2 fugacity in the range of one μatm (typical low latitude water) up to several μatm (about 5 μatm for typical high latitude water).

Total borate (TB) is assumed to be linearly related to chlorinity [*Uppström*, 1974]. The salinity to chlorinity ratio of 1.80655 as given by *UNESCO* [1966] together with the relative atomic mass of B of 10.81 u leads to the following relation between total borate in mol per kg of solution and salinity:

$$
TB = 1.188\,10^{-5} \cdot S \qquad \text{(A.11)}
$$

Chemical equilibrium constants: The carbonate system in the model is governed by the chemical equilibria of CO_2 exchange at the air sea interface, the dissociation of carbonic, boric, silicic and phosphoric acid and of water. The non-carbonic dissociation constants are used in order to account for the non-carbon fractions in TA, as shown in Eq. A.8 to A.11).

The CO_2 solubility, K_0, is defined as

$$
K_0 = \frac{[\mathrm{CO_2}]}{fCO_2} \qquad \text{(A.12)}
$$

where fCO_2 is the fugacity of CO_2 [*Weiss*, 1974] and $[CO_2]$ is expressed in mol per kg sea water.

The following definitions of the equilibrium equations are related to the sea-water scale (SWS), i. e. the concentrations are stoichiometric concentrations including complex formation with other constituents [*Dickson*, 1984]. The first (K_1) and second (K_2) dissociation constant for carbonic acid, the dissociation constant for boric acid (K_b), water (K_w), the first, second and third dissociation constant for phosphoric acid (K_{P_1}, K_{P_2},K_{P_3}) and for silicic acid (K_{Si}) are defined below.

$$K_1 = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} \tag{A.13}$$

$$K_2 = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} \tag{A.14}$$

$$K_b = \frac{[H^+]\,[B(OH)_4^-]}{[B(OH)_3]} \tag{A.15}$$

$$K_w = [H^+][OH^-] \tag{A.16}$$

$$K_{P_1} = \frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]} \tag{A.17}$$

$$K_{P_2} = \frac{[H^+]\,[HPO_4^{2-}]}{[H_2PO_4^-]} \tag{A.18}$$

$$K_{P_3} = \frac{[H^+]\,[PO_4^{3-}]}{[HPO_4^{2-}]} \tag{A.19}$$

$$K_{Si} = \frac{[H^+]\,[Si(OH)_3O^-]}{[Si(OH)_4]} \tag{A.20}$$

Equilibrium constants as a function of temperature and salinity: For convenience, we summarize the description of equilibrium constants as functions of temperature and salinity in Tab. 4 (When using such functions readers should cite the original reference as given in the table caption). Unless explicitly mentioned, the symbol T represents absolute temperature in units of K, S the salinity, and the dissociation constants are given in units of mol per kg of solution.

The CO_2 solubility K_0 [*Weiss*, 1974] can be written as a function of temperature T and salinity S

$$\begin{aligned} \ln K_0 &= A_1 + \frac{A_2}{h} + A_3 \ln(h) + \\ &\quad S \cdot (B_1 + (B_2 + B_3 \cdot h) \cdot h) \end{aligned} \tag{A.21}$$

where

A_1 = -60.2409 $\quad A_2$ = 93.4517 $\quad A_3$ = 23.3585
B_1 = 0.023517 $\quad B_2$ = -0.023656 $\quad B_3$ = 0.0047036
$h = T/100$

K_0 is given in mol/(kg · atm), T in K and S in psu.

For convenience the function $\mathcal{H}$ is introduced:

$$\begin{aligned} \mathcal{H}(T,S) &= t_0 + t_{0.5}S^{0.5} + t_1 S + t_{1.5}S^{1.5} + t_2 S^2 \\ t_i &= c_{i,0} + \frac{c_{i,1}}{T} + c_{i,2}\ln(T) + c_{i,3}T \\ i &\in \{0,\ 0.5,\ 1,\ 1.5,\ 2\} \end{aligned} \tag{A.22}$$

where "ln" as used here is the logarithm to the basis e. The temperature T is given in K, the salinity S in psu. The coefficients which correspond to the appropriate dissociation constant are given in Table 4.

The dissociation constants $\mathrm{K_1}$, $\mathrm{K_2}$, $\mathrm{K_W}$, $\mathrm{K_{P_1}}$, $\mathrm{K_{P_2}}$, and $\mathrm{K_{P_3}}$ are expressed as

$$\ln(K) = \mathcal{H}(T,S) \tag{A.23}$$

The dissociation constants of silicic and boric acids need special attention. The dissociation constant of silicic acid as given by *Millero* [1995] is related to molal units and has therefore to be converted to units of mol per kg of solution:

$$\begin{aligned} \ln(K_{Si}) &= (1 - 1.005 \cdot 10^{-3}\, S) \cdot \mathcal{H}(T, I_m) \\ I_m &= \frac{I}{1 - 1.005 \cdot 10^{-3}\, S} \end{aligned} \tag{A.24}$$

where the ionic strength of natural sea water (kg per solution (sea water)) is given by the relation [*Millero*, 1974]

$$I = 1.99273 \cdot 10^{-2}\, \frac{\mathrm{C^2\,mol}}{\mathrm{kg\ psu}} \cdot S \tag{A.25}$$

The boric acid constant as given by *Dickson* [1990] is related to the total hydrogen ion scale. It has therefore to be converted to the pH(SWS) scale by considering species of sulfur and fluorine. The dissociation constant of boric acid related to the total hydrogen ion concentration scale, i. e. sea-water scale (SWS) without HF, is given as

$$\ln(K_{b,\text{ no HF}}) = \mathcal{H}(T,S) \tag{A.26}$$

The borate dissociation constant is then converted to the sea-water scale by taking into account the different hydro-fluoride species:

$$K_b = K_{b,\text{ no HF}}\, \frac{1 + \beta_{\mathrm{HSO_4^-}}\,(\mathrm{TSO_4}) + \beta_{\mathrm{HF}}\,(\mathrm{TF})}{1 + \beta_{\mathrm{HSO_4^-}}\,(\mathrm{TSO_4})_{af}} \tag{A.27}$$

where $(\mathrm{TSO_4})$ and (TF) are total sulfate and fluorine in molal units and the β terms are formation constants. The β terms related to molal units can be calculated by using following equations (c. f. [*Khoo et al.*, 1977] and [*Dickson and Riley*, 1979]):

$$\log(\beta_{\mathrm{HSO_4^-}}) = \frac{647.59}{T} - 6.3451 + 0.019085\,T - 0.5208\sqrt{I_m} \quad (A.28)$$

$$\ln(\beta_{\mathrm{HF}}) = \frac{-1590.2}{T} + 12.641 - 1.525\sqrt{I_m} \quad (A.29)$$

Here 'log' refers to the basis 10, and 'ln' to the basis e. Total sulphate (TSO4) and total fluorine (TF) for natural sea water are given as a function of salinity: (see [*Dickson and Millero*, 1987] and Equation A.1):

$$(\mathrm{TSO_4}) = \frac{8.069 \cdot 10^{-4}\,S}{1 - 1.005 \cdot 10^{-3}\,S} \quad (A.30)$$

$$(\mathrm{TF}) = \frac{2.0 \cdot 10^{-6}\,S}{1 - 1.005 \cdot 10^{-3} \cdot S} \quad (A.31)$$

and the total sulphate $(\mathrm{TSO_4})_{af}$ of the artificial sea water used by *Dickson* [1990] can be calculated by

$$(\mathrm{TSO_4})_{af} = \frac{(\mathrm{Na_2SO_4})_{35}}{I_{af}(S=35)} \cdot I_{af} \quad (A.32)$$

where the $\mathrm{Na_2SO_4}$ molality at S=35 psu and the ionic strength of Dickson's artificial sea water are given as

$$(\mathrm{Na_2SO_4})_{35} = 2.927\,10^{-2}\ \mathrm{mol/kg\text{-}solvent} \quad (A.33)$$

$$I_{af} = \frac{19.919 \cdot S}{1000 - 1.00198 \cdot S} \quad (A.34)$$

Calculation of fCO_2 and the CO_2 concentration of surface seawater:

In the following paragraphs the approach used at Bern to calculate the CO_2 concentration $[CO_2]$ is described. The total alkalinity TA and the total concentrations TCO_2, TSi, TB and TP as well as temperature and salinity are known input variables. Equilibrium constants are functions of temperature and salinity as described in the previous sections. The CO_2 fugacity fCO_2 is calculated in two steps. First, aquatic CO_2 ($[CO_2]$) is determined; then $[CO_2]$ is divided by the solubility (Eq. A.12) to obtain fCO_2. $[CO_2]$ is a non-linear function of the specified concentrations and the equilibrium constants and can not be calculated analytically. We applied the Newton algorithm as an iterative numerical scheme to solve Eq. A.42 derived below. An initial guess of $[CO_2]$ has to be specified for the iteration. This guess is calculated by solving approximative analytical equations of the carbonate systems (Eqs. A.35 and A.35). Then, the iteration converges fast in the range of interest.

Initial guess for $[CO_2]$: The largest contribution to total alkalinity stems from the carbonate alkalinity A_c. With the help of the approximation "TA $\approx A_c$" (c. f. Eq. A.6), we obtain then by applying Eqs A.2, A.13, and A.14 the following initial guess for $[\mathrm{CO_2}]$:

$$
\begin{aligned}
d_1 &:= 1 - 4\frac{K_2}{K_1} \\
d_2 &:= d_1 A_c - TCO_2 \\
\mathcal{D} &:= (d_2)^2 + 4\,\frac{K_2}{K_1}\,d_1\,(A_c)^2 \\
[\mathrm{CO_3^{2-}}] &= \frac{d_2 + \sqrt{\mathcal{D}}}{2d_1} \\
[\mathrm{CO_2}] &= \frac{K_2}{K_1}\frac{\left(A_c - 2[\mathrm{CO_3^{2-}}]\right)^2}{[\mathrm{CO_3^{2-}}]} \qquad \text{(A.35)}
\end{aligned}
$$

Calculation of $[CO_2]$: In the following, an equation is derived where TA is expressed as a function of $[\mathrm{CO_2}]$, $\mathrm{TCO_2}$, TB, TSi, TP and the equilibrium constants. The unknown $[\mathrm{CO_2}]$ is then related to known quantities only. We define for convenience:

$$
\begin{aligned}
\bar{K} &:= \sqrt{\frac{K_1}{K_2}} \\
\bar{S} &:= \sqrt{K_1 K_2} \\
X &:= -\frac{\bar{K}}{2} + \sqrt{\frac{1}{4}\bar{K}^2 + \frac{TCO_2}{[\mathrm{CO_2}]} - 1} \qquad \left(= \sqrt{\frac{[\mathrm{CO_3^{2-}}]}{[\mathrm{CO_2}]}}\right) \\
h_2 &:= 1 + \frac{[\mathrm{H^+}]}{K_{P_2}} + \frac{K_{P_3}}{[\mathrm{H^+}]} \\
h_3 &:= 1 + \frac{[\mathrm{H^+}]}{K_{P_3}} + \frac{[\mathrm{H^+}]^2}{K_{P_2}\,K_{P_3}}
\end{aligned}
$$

and the relation

$$
[\mathrm{H^+}] = \frac{\bar{S}}{X}. \qquad \text{(A.36)}
$$

Then the single contributions to the total alkalinity are expressed as a function of the $\mathrm{CO_2}$ concentration, the measured quantities and the dissociation constants:

$$
\begin{aligned}
A_c &= [\mathrm{CO_2}]\cdot(\bar{K} + 2X)\cdot X \qquad \text{(A.37)} \\
A_b &= TB \cdot \frac{K_b}{[\mathrm{H^+}] + K_b} \qquad \text{(A.38)} \\
A_w &= UF \cdot \left(\frac{K_w}{[\mathrm{H^+}]} - [\mathrm{H^+}]\right) \qquad \text{(A.39)}
\end{aligned}
$$

$$A_{Si} = TSi \cdot \frac{K_{Si}}{[\mathrm{H}^+] + K_{Si}} \quad \text{(A.40)}$$

$$A_P = TP \cdot \left(\frac{1}{h_2} + \frac{2}{h_3}\right) \quad \text{(A.41)}$$

UF is a factor for unit conversion and equals 1 if concentrations are in mol/kg-solution.

$[CO_2]$ is then calculated by finding the root of the equation

$$TA - A_c - A_b - A_{Si} - A_P - A_w = 0 \quad \text{(A.42)}$$

and by applying Eq. A.35 as an initial guess.

The concentration $[H_3PO_4]$ has been neglected . This is a reasonable simplification, because for sea-water conditions the pH value is about 8, the value of $\mathrm{K}_{\mathrm{P}_1}$ is in the range of 10^{-2}, and thus the $[H_3PO_4]$ to $[H_2PO_4^-]$ ratio is only about 10^{-6}.

The above relations have been developed for the pH(SWS) scales and all concentrations and dissociation constants are expressed in mol/kg-solution. However, in ocean circulation models concentrations are usually expressed per volume, e.g. in mol m^{-3}-solution. For convenience, a unit conversion factor, UF, has been introduced in A.39. This allows one to specify the input variables TCO_2, TA, TB, TSi, and TP for Eq. A.42 in different units without changing the definition of the dissociation constants and $[\mathrm{H}^+]$ in units mol/kg-solution. Note that the output of the iteration, $[CO_2]$, is then defined in the same units as the input concentrations. This requires according adaption of the CO_2 solubility when evaluating Eq. A.12 to calculate fCO_2. UF equals the seawater density in kg m^{-3} for input concentrations in mol m^{-3}; UF=10^6 for the input in μmol/kg-solution.

B fCO_2 error of method $\mathcal{M}_{xCO_2}$

Here, the equations used to calculate the uncertainties in fugacity, $\Delta fCO_2(T_s)$, are described for method $\mathcal{M}_{xCO_2}$. The overall error in fCO_2 at in situ temperature includes the uncertainty $\Delta \widehat{fCO_2}$ of the fugacity determined at the equilibrator temperature $\widehat{T}$, and the uncertainty, $\Delta\delta fCO_2$, arising from the correction due to the difference between equilibrator temperature, $\widehat{T}$, and the in situ temperature, T_s. The error of fCO_2 is derived from Equation 2.4 and 2.5 and is given as

$$\begin{aligned}(\Delta fCO_2)^2 = & \sum_{C_i \in \mathcal{C}} \left(\left[\left.\frac{\partial fCO_2}{\partial C_i}\right|_{T_s} - \left.\frac{\partial fCO_2}{\partial C_i}\right|_{\widehat{T}} \right] \cdot \Delta C_i \right)^2 \\ & + \sum_{K_i \in \mathcal{K}} (\Delta F_{K_i})^2 \\ & + \sum_{K_i \in \mathcal{K}} \left(\left.\frac{\partial fCO_2}{\partial K_i}\right|_{T_s} \left.\frac{\partial K_i}{\partial T_s}\right|_{T_s} \cdot \Delta T_s \right)^2 \end{aligned} \quad \text{(B.1)}$$

$$
\begin{aligned}
&+ \left(\frac{d\widehat{fCO_2}}{d\widehat{T}} - \sum_{K_i \in \mathcal{K}} \frac{\partial fCO_2}{\partial K_i}\bigg|_{\widehat{T}} \frac{\partial K_i}{\partial T}\bigg|_{\widehat{T}} \right)^2 \cdot \left(\Delta\widehat{T}\right)^2 \\
&+ \left(\frac{d\widehat{fCO_2}}{dS} + \sum_{K_i \in \mathcal{K}} \left[\frac{\partial fCO_2}{\partial K_i}\bigg|_{T_s} \frac{\partial K_i}{\partial S}\bigg|_{T_s} - \frac{\partial fCO_2}{\partial K_i}\bigg|_{\widehat{T}} \frac{\partial K_i}{\partial S}\bigg|_{\widehat{T}} \right] \right. \\
&+ \left. \frac{\partial fCO_2}{\partial TB}\bigg|_{T_s} \frac{dTB}{dS} - \frac{\partial fCO_2}{\partial TB}\bigg|_{\widehat{T}} \frac{dTB}{dS} \right)^2 \cdot (\Delta S)^2 \\
&+ \left(\frac{\partial\widehat{fCO_2}}{\partial xCO_2} \cdot \Delta xCO_2 \right)^2 \\
&+ \left(\frac{\partial\widehat{fCO_2}}{\partial e_w} \cdot \Delta e_w \right)^2 \\
&+ \left(\frac{\partial\widehat{fCO_2}}{\partial K_f} \cdot \Delta K_f \right)^2 \\
&+ \left(\frac{d\widehat{fCO_2}}{dP_{atm}} \cdot \Delta P_{atm} \right)^2
\end{aligned}
$$

The first sum of the right hand side describe the errors due to uncertainties in the concentration measurements of TA, TCO_2, TSi, TP, and in the relationship between TB and salinity; the second holds the uncertainty due to uncertainties in the equilibrium constants, ΔF_{K_i}. The sets $\mathcal{K}$ and $\mathcal{C}$ include the 8 equilibrium constants and the 5 concentrations required in the applied chemistry model (appendix A). The fCO_2 uncertainty due to the dissociation constants needs further consideration and is explained below. The next terms describe the dependency of ΔfCO_2 on SST and reference temperature, and salinity; the last terms handle the error due to the CO_2 mole fraction, the water vapor pressure, the fugacity factor, and the atmospheric pressure at equilibrator conditions.

The fCO_2 error due to the dissociation constants: All the important dissociation constants have been determined by laboratory measurements at about 5 °C intervals (c. f.[*Roy et al.*, 1993],[*Dickson*, 1990], [*Dickson and Riley*, 1979] and [*Weiss*, 1974]). These values are then fitted to obtain continuous functions of T and S. Thus, the uncertainties in equilibrium constants evaluated at two different temperatures are dependent for small temperature differences and independent for large differences. We assume that the errors arising from uncertainties in the equilibrium constants at the two temperature, $\widehat{T}$ and T_s, are statistically independent, if the difference in the temperatures are larger than 20°C. Otherwise, we interpolate linearly between formulation describing a dependency of the two errors, $\mathit{\Delta F}_{dep}$, and the independent formulation, $\mathit{\Delta F}_{ind}$:

$$\begin{array}{ll} \Delta F_{K_i} = \Delta F_{dep} + (\Delta F_{ind} - \Delta F_{dep}) \cdot \frac{\left|T_s - \widehat{T}\right|}{20\ ^\circ\mathrm{C}} & \left|T_s - \widehat{T}\right| < 20\ ^\circ\mathrm{C} \\ \Delta F_{K_i} = \Delta F_{ind} & \left|T_s - \widehat{T}\right| \geq 20\ ^\circ\mathrm{C} \end{array} \tag{B.2}$$

The independent formulation, ΔF_{ind}, is:

$$\Delta F_{ind}(K_i) = \left\{ \left(\left.\frac{\partial fCO_2}{\partial K_i}\right|_{T_s} \cdot \Delta K_i(T_s, S) \right)^2 + \left(\left.\frac{\partial fCO_2}{\partial K_i}\right|_{\widehat{T}} \cdot \Delta K_i(\widehat{T}, S) \right)^2 \right\}^{0.5} \tag{B.3}$$

The dependent formulation, ΔF_{dep}, is [1]:

$$\Delta F_{dep}(K_i) = \left| \left.\frac{\partial fCO_2}{\partial K_i}\right|_{T_s} \cdot \Delta K_i(T_s, S) - \left.\frac{\partial fCO_2}{\partial K_i}\right|_{\widehat{T}} \cdot \Delta K_i(\widehat{T}, S) \right| \tag{B.4}$$

The error of the dissociation constant is given in literature as an error of the pK_i value. Therefore the relationship

$$\frac{\Delta K_i}{K_i} \approx \ln(10) \cdot \Delta pK_i \tag{B.5}$$

is used to evaluate the error due to the dissociation constant K_i itself.

Finally, it may be noted that for $\widehat{T}$ equal T_s the r.h.s. terms concerning the concentrations, the dissociation constants and partially the salinity in equation B.1 cancel, but not the uncertainties arising from ΔT_s and $\Delta\widehat{T}$. This because T_s and $\widehat{T}$ are two independent measured values.

[1] The fCO_2 uncertainty ΔF_{ind} due to all independent error terms is always bigger than ΔF_{dep}. This is because the sign of the partial derivative of the fugacity with respect to K_i is *for all temperatures* of interest always the same (For increasing K_0 and K_1 the fugacity is decreasing, while for K_2, K_b, K_w, K_{Si} and K_{P_3} the opposite is true). Note, that the dependent term vanishes for $\widehat{T}=T_s$ in contrast to the independent one.

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Quantity	Symbol	2 σ error	Reference
Concentrations:			
Total alkalinity	TA	4 μeq/kg	[*Millero*, 1995]
Total CO_2	TCO_2	2 μmol/kg	[*Millero*, 1995]
Total borate	TB	4.7%	[*Uppström*, 1974]
Total silicate	TSi	1%	
Total phosphate	TP	1%	
Equilibrium constants:			
CO_2 solubility	pK_0	0.002	[*Weiss*, 1974]
$[CO_2] \rightleftharpoons [HCO_3^-] + [H^+]$	pK_1	0.007	[*Millero*, 1995]
$[HCO_3^-] \rightleftharpoons [CO_3^{2-}] + [H^+]$	pK_2	0.006	[*Millero*, 1995]
$[B(OH)_3] \rightleftharpoons [B(OH)_4^-] + [H^+]$	pK_b	0.0036	[*Dickson*, 1990]
$[H_2O] \rightleftharpoons [OH^-] + [H^+]$	pK_w	0.009	[*Millero*, 1995]
$[SiO_2] \rightleftharpoons [Si(OH)_3O^-] + [H^+]$	pK_{Si}	0.04	[*Millero*, 1995]
$[H_2PO_4^-] \rightleftharpoons [HPO_4^{2-}] + [H^+]$	pK_{P_2}	0.06	[*Millero*, 1995]
$[HPO_4^{2-}] \rightleftharpoons [PO_4^{3-}] + [H^+]$	pK_{P_3}	0.4	[*Millero*, 1995]
Others:			
Sea surface temperature	SST	0.2 °C	
Salinity	S	0.1	
Only used for $\mathcal{M}_{xCO_2}$:			
CO_2 mole fraction (dry air)	xCO_2	0.6 ppm	
Equilibrator temperature	$\widehat{T}$	0.01 °C	
Water vapour pressure	e_w	0.1%	
Fugacity factor	K_f	0.1%	
Total atmospheric pressure	P_{atm}	0.05%	

Table 1: 2-σ uncertainties of parameters used in the error propagation calculations. Uncertainties in TCO_2, TA, TB, and in the equilibrium constants of the eight chemical reactions considered in this work were taken from literature. Relatively large uncertainties in the sea surface temperature and salinity measurement were adapted, thereby taking into account inertia of instruments and small scale temperature and salinity variations in the water column.

	pK_1	pK_2	Data
Residuals	≈ 0.02	≈ 0.04	[*Goyet and Poisson*, 1989][a]
	≈ 0.02	≈ 0.04	[*Goyet and Poisson*, 1989] and [*Hansson*, 1973][a]
	≈ 0.009	≈ 0.004	[*Roy et al.*, 1993][b]
1-σ uncertainty:			
Goodnes of the fit (1-σ)	0.0065	0.011	[*Goyet and Poisson*, 1989][a]
Goodnes of the fit (1-σ)	0.0055	0.010	[*Goyet and Poisson*, 1989] and [*Hansson*, 1973][a]
Standard deviation of the fit	0.0042	0.0061	[*Roy et al.*, 1993][b]
Standard error of the fit	0.0035	0.003	[*Roy et al.*, 1993][c]
Overall standard error	0.0012	0.0025	[*Roy et al.*, 1993] and [*Goyet and Poisson*, 1989][c]

Table 2: Residuals and estimated uncertainties of the carbonic acid dissociation constants (pK_1, pK_2) for three published data sets ([*Hansson*, 1973],[*Goyet and Poisson*, 1989],[*Roy et al.*, 1993]) and combinations of these sets. The data points of a set have been fitted to express the dissociation constants as analytical functions of sea surface temperature and salinity. The residuals are the difference between the analytical function and individual data points. Values are from (superscript a) [*Goyet and Poisson*, 1989], (b) [*Roy et al.*, 1993] and (c) [*Millero*, 1995]. Estimated uncertainties vary by up to a factor of five. For this work, the 'standard errors of the fit' as calculated by [*Millero*, 1995] for the data published by [*Roy et al.*, 1993] were used as a typical 1-σ uncertainties of pK_1 and pK_2 (Tab. 1).

	TA μeq/kg	TCO_2 μmol/kg	TB=TB(S) μmol/kg	TSi μmol/kg	TP μmol/kg	S
Warm Sample	2300	2000	415.8	5.0	0.35	35.0
Cold Sample	2350	2200	415.8	30.0	1.30	35.0

Table 3: Concentrations of two artificial sea water samples representing typical low- (Warm Sample) and high-latitude (Cold Sample) surface waters. The two samples are used to investigate uncertainties in fCO_2 for different measurement strategies. 'Measured' TCO_2 and TA values were calculated as zonal averages from the GEOSECS and TTO data sampled in the upper 75 meter of the water column. The 5 Celsius isoline was taken as the border between low and high latitudes. Total borate was calculated as a function of salinity ([*Uppström*, 1974]).

Coefficients $c_{0,i}$ of t_0 for all the dissociation constants:

	$c_{0,0}$	$c_{0,1}$	$c_{0,2}$	$c_{0,3}$
K_1	2.18867	–2275.0360	–1.468591	–
K_2	–0.84226	–3741.1288	–1.437139	–
K_b	148.0248	–8966.90	–24.4344	–
K_w	148.9802	–13847.26	–23.6521	–
K_{Si}	117.40	–8904.2	–19.334	–
K_{P_1}	115.54	–4576.752	–18.453	–
K_{P_2}	172.1033	–8814.715	–27.927	–
K_{P_3}	–18.126	–3070.75	–	–

Coefficients $c_{0.5,i}$ of $t_{0.5}$ for all the dissociation constants:

	$c_{0.5,0}$	$c_{0.5,1}$	$c_{0.5,2}$	$c_{0.5,3}$
K_1	–0.138681	–9.33291	–	–
K_2	–0.128417	–24.41239	–	–
K_b	137.1942	–2890.53	–25.085	0.053105
K_w	–5.977	118.67	1.0495	–
K_{Si}	3.5913	–458.79	–	–
K_{P_1}	0.69171	–106.736	–	–
K_{P_2}	1.3566	–160.340	–	–
K_{P_3}	2.81197	17.27039	–	–

Coefficients $c_{1,i}$ of t_1 for all the dissociation constants:

	$c_{1,0}$	$c_{1,1}$	$c_{1,2}$	$c_{1,3}$
K_1	0.0726483	–	–	–
K_2	0.1195308	–	–	–
K_b	1.62142	–77.942	–0.2474	–
K_w	–0.01615	–	–	–
K_{Si}	–1.5998	188.74	–	–
K_{P_1}	–0.01844	–0.65643	–	–
K_{P_2}	–0.05778	0.37335	–	–
K_{P_3}	–0.09984	–44.99486	–	–

Coefficients $c_{1.5,i}$ of $t_{1.5}$ only different from zero for K_1, K_2, K_b.

	$c_{1.5,0}$	$c_{1.5,1}$	$c_{1.5,2}$	$c_{1.5,3}$
K_1	–0.00574938	–	–	–
K_2	–0.00912840	–	–	–
K_b	–	1.728	–	–

Coefficients $c_{2,i}$ of t_2 only different from zero for K_b and K_{Si}:

	$c_{2,0}$	$c_{2,1}$	$c_{2,2}$	$c_{2,3}$
K_b	–	–0.0996	–	–
K_{Si}	0.07871	–12.1652	–	–

Table 4: Coefficients of $\mathcal{H}$ which are used to calculate the dissociation constants (see equations A.23, A.24 and A.26). The definition of the function $\mathcal{H}$ is given in Eq. A.22. For references see ee Tab. 5.

Constant	Reference	Data
K_0	*Weiss* [1974]	
K_1, K_2	*Millero* [1995]	combined measurements from
		Roy et al. [1993]
		Goyet and Poisson [1989]
K_b	*Dickson* [1990]	
K_W	*Millero* [1995]	combined measurements from
		Hansson [1973]
		Culberson and Pytkowicz [1973]
		Dickson and Riley [1979]
K_{P_2}, K_{P_3}	*Millero* [1995]	
K_{Si}	*Millero* [1995]	

Table 5: References for equilibrium constants as used in the seawater carbon chemistry model of this work. Published values for the carbonic acid constants K_1 and K_2 are based on data published by *Goyet and Poisson* [1989] and *Roy et al.* [1993]. K_W is based on measurements from *Hansson* [1973], *Culberson and Pytkowicz* [1973], and *Dickson and Riley* [1979]. Published values of K_b were adapted to the pH(SWS) scale by including the influence of fluoride (see Equation A.27); K_{Si} was converted from molality (mol per kg of solvent) into units of mol per kg of solution.

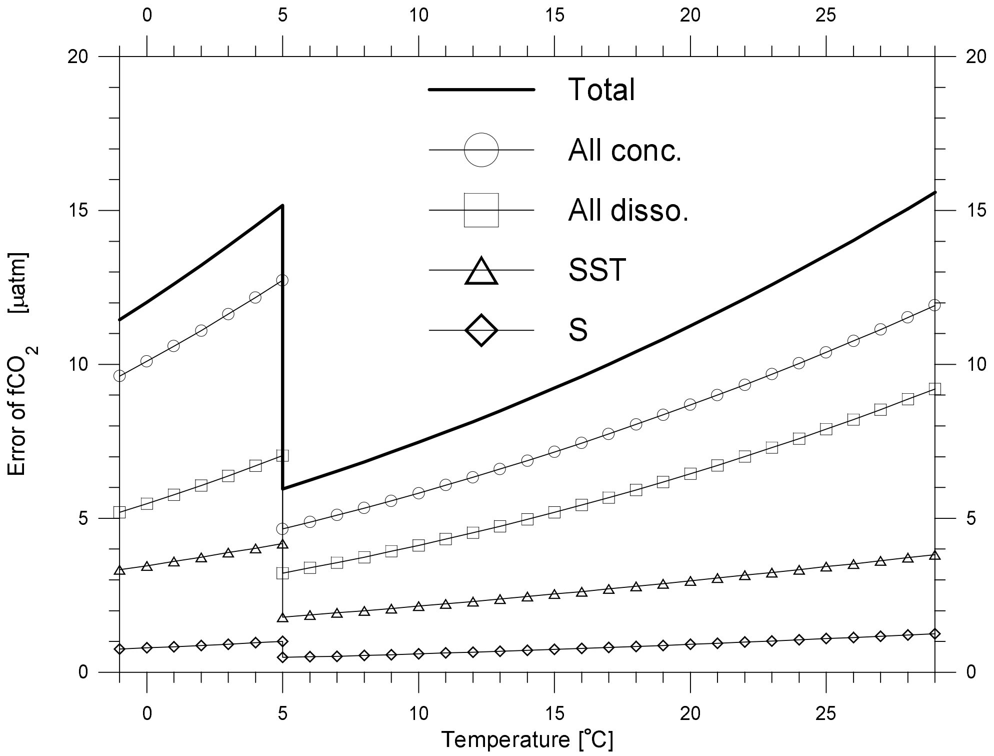

Figure 1: 2-σ uncertainties in fCO_2 determined from measured concentrations (method $\mathcal{M}_{DIC}$) as a function of in situ temperature for the two water samples defined in Tab. 3. Uncertainties were analyzed for a temperature range of -1 to 5 °C for the Cold Sample and of 5 to 30 °C for the Warm Sample. Errors arising from uncertainties in sea surface temperature (triangle) and salinity (diamond), the concentrations of TCO_2, TA, TB, TP, and TSi (circles), and from uncertainties in the eight equilibrium constants (squares) are plotted separately. The total uncertainty (thick solid line) was obtained by quadratic error addition.

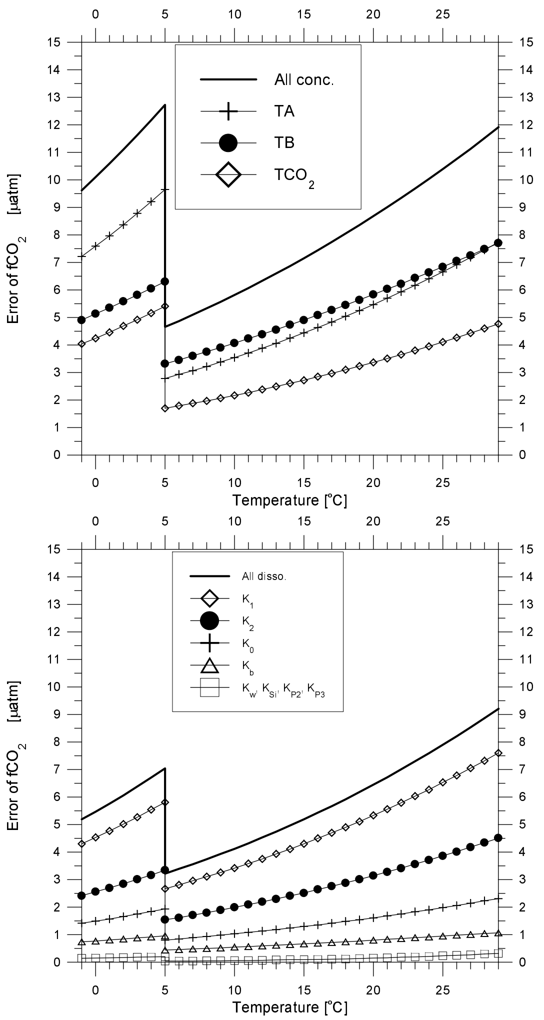

Figure 2: a) 2-σ uncertainties in fCO_2 determined from measured concentrations (method $\mathcal{M}_{DIC}$) as a function of in situ temperature for the two water samples defined in Tab. 3. Uncertainties were analyzed for a temperature range of -1 to 5 °C for the Cold Sample and of 5 to 30 °C for the Warm Sample. The solid lines shows the 2-σ error in fCO_2 due to uncertainties in five measured concentrations as obtained by Gaussian error propagation (circles in Fig. 1). Errors arising from uncertainties in TCO_2, TA, and the TB - S relationship are plotted separately. Uncertainties in measured TSi and TP are not relevant. b) As a) but errors in fCO_2 are shown for uncertainties in the eight equilibrium constants of the reactions summarized in Tab. 1. The thick solid line corresponds to the squares in Fig. 1.

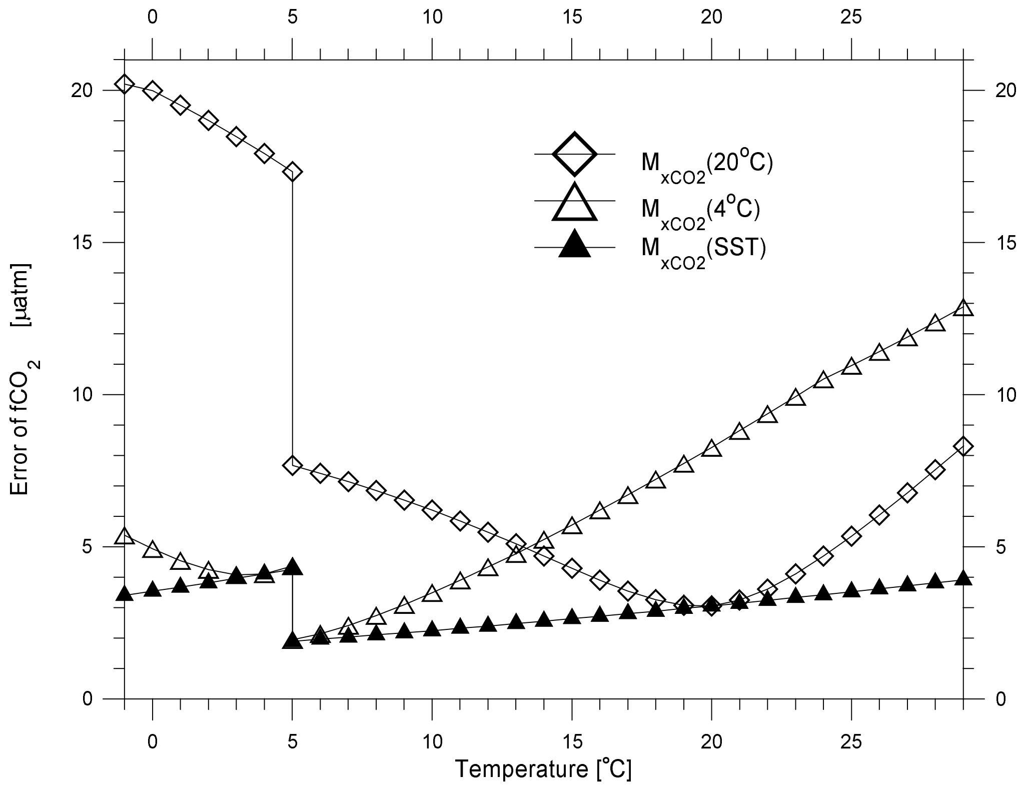

Figure 3: 2-σ uncertainties in fCO_2 as a function of the in situ temperature (SST) for the two water samples defined in Tab. 3. It is assumed that fCO_2 is determined by mole fraction measurements on air equilibrated with the sample at temperature $\widehat{T}$ (method $\mathcal{M}_{xCO_2}$). Uncertainties were analyzed for a temperature range of -1 to 5 °C for the Cold Sample and of 5 to 30 °C for the Warm Sample. The temperature of the analyzed air ($\widehat{T}$) is assumed to be equal to SST, 4 °C or 20 °C.

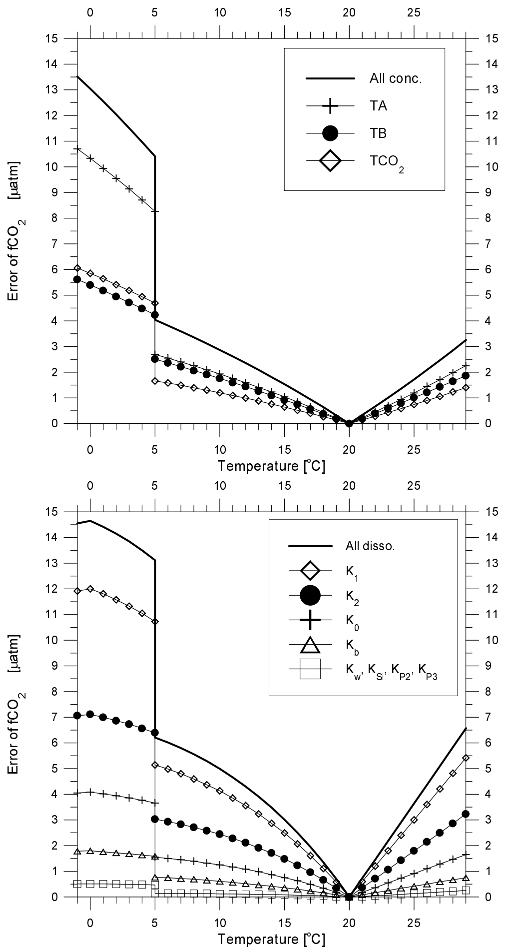

Figure 4: a) 2-σ uncertainties in fCO_2 as a function of in situ temperature and as arising due to uncertainties in measured concentrations of TCO_2, TA, TP, TSi, and the TB- S relationship. fCO_2 was determined by mole fraction measurements (method $\mathcal{M}_{xCO_2}$) at air equilibrated with the sample at $\widehat{T}$= 20 °C. A chemistry model is used to correct between the temperature difference in the equilibrator ($\widehat{T}$) and the in situ temperature. The concentrations of TCO_2, TA, TB, TP, and TSi as well as eight equilibrium constants were used as input into the model. Uncertainties were analyzed for a temperature range of -1 to 5 °C for the Cold Sample and of 5 to 30 °C for the Warm Sample as defined in Tab. 3. Errors arising from uncertainties in TCO_2, TA, TB are plotted separately. Uncertainties in measured TSi and TP are not relevant. The solid line shows the total uncertainties in fCO_2 due to all five concentration measurements as obtained by quadratic error addition. b) As a) but errors in fCO_2 are shown for uncertainties in the eight equilibrium constants summarized in Tab. 1

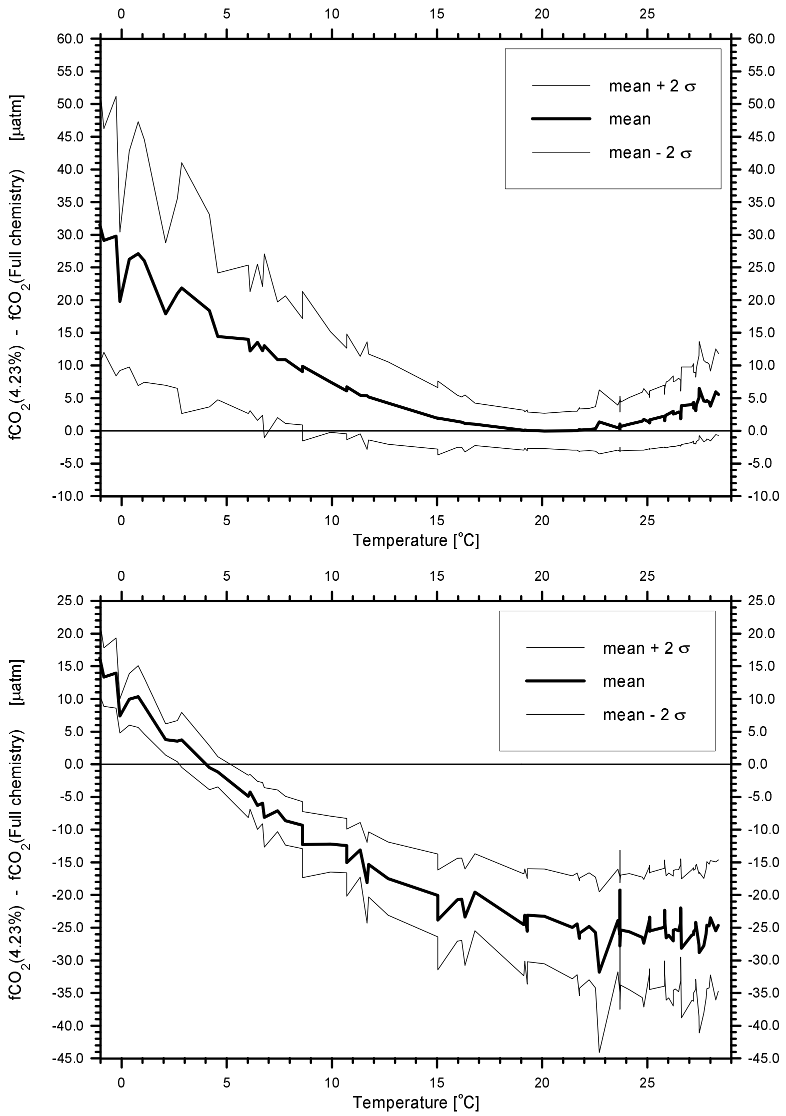

Figure 5: a) Difference in estimated fCO_2 for two different methods to correct between in situ temperature and equilibrator temperature ($\widehat{T}$). It is assumed that fCO_2 was determined by measuring the mole fraction on air equilibrated with a sample at 20 °C(method $\mathcal{M}_{xCO_2}$). The zonally averaged GEOSECS and TTO surface values were used as described in the text. In one method ($\mathcal{M}_{xCO_2}$) the chemistry model outlined in the Appendix A was invoked to correct for the temperature difference between SST and equilibrator. Alternatively, fCO_2 is assumed to vary exponentially with temperature (4.23 %) according to Eq. 1.2. The thick solid line was obtained by connecting the values as calculated for the zonally averaged data (see text). The two thin solid lines give the 2-σ uncertainty band as calculated by error propagation using the chemistry model outlined in Appendix A. b) As a) but for an equilibrator temperature ($\widehat{T}$) of 4 °C.

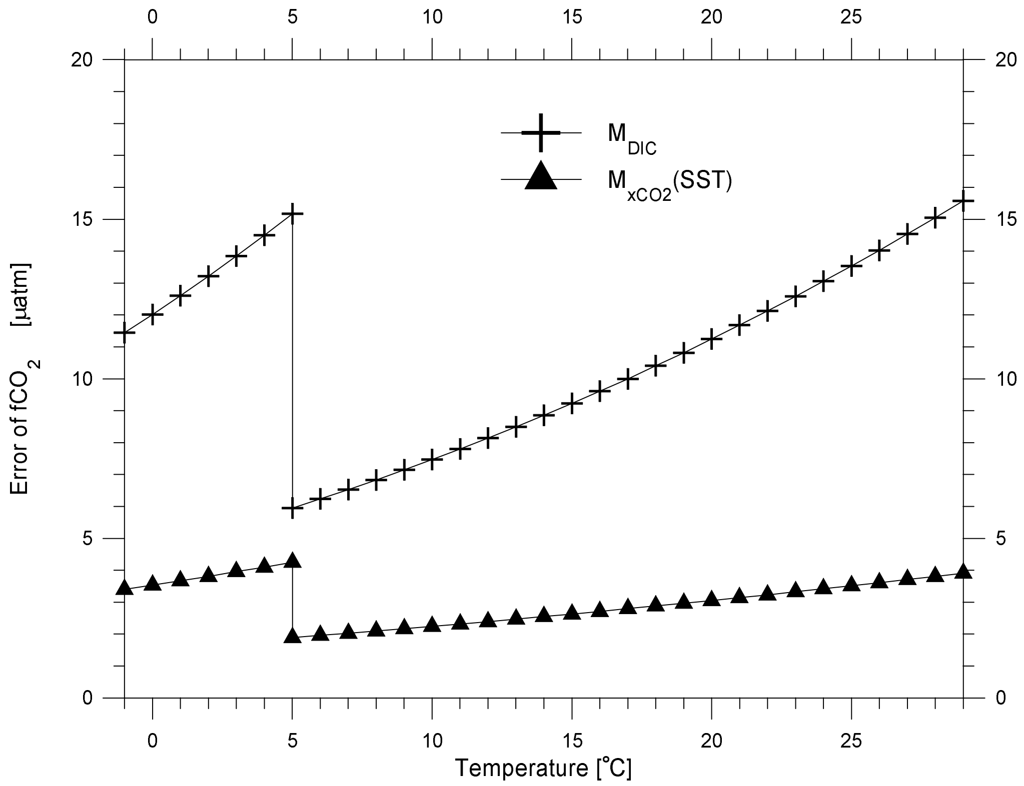

Figure 6: 2-σ uncertainties in fCO_2 determined from measured concentrations (method $\mathcal{M}_{DIC}$) and from mole fraction measurements (method $\mathcal{M}_{xCO_2}$). Uncertainties are shown as a function of in situ temperature for the two water samples defined in Tab. 3. The optimal case occurs when the in-situ temperature and the temperature of the analyzed air are equal. Uncertainties were analyzed for a temperature range of -1 to 5 °C for the Cold Sample and of 5 to 30 °C for the Warm Sample.

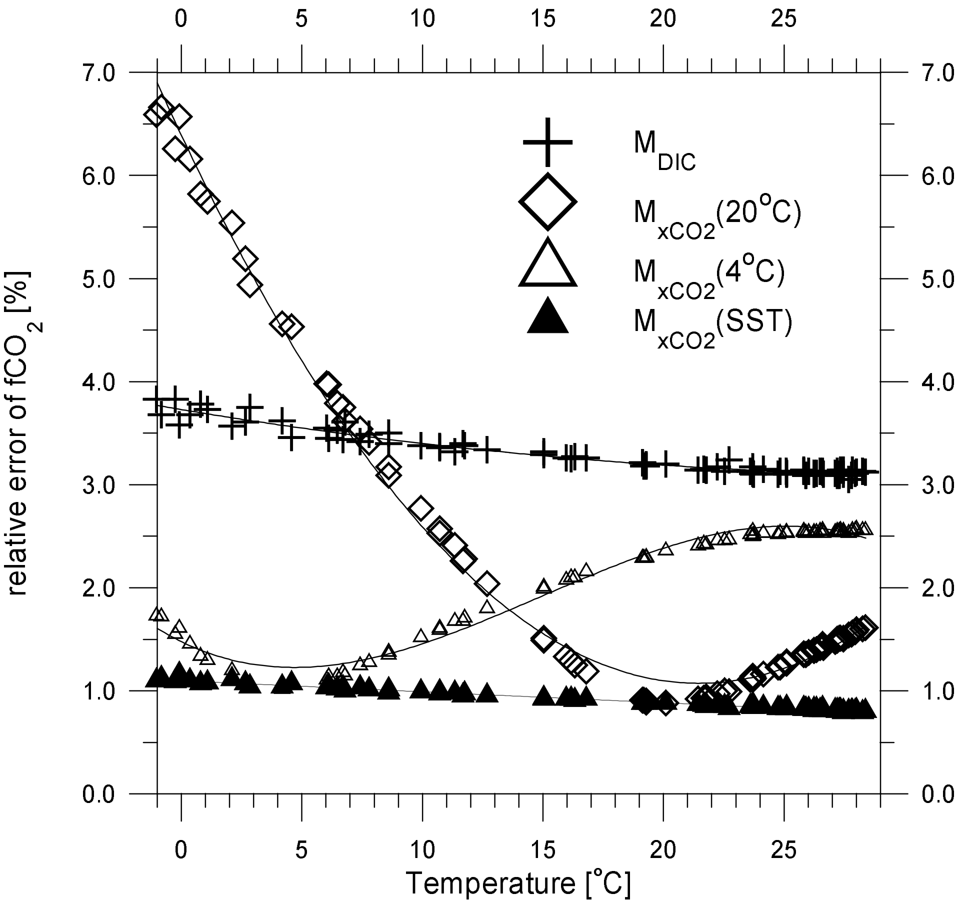

Figure 7: 2-σ uncertainty in fCO_2 as a function of temperature. Individual symbols represent zonally averaged surface values for 5-degree latitude belts for the Pacific, Atlantic and Indian Ocean as calculated from the GEOSECS and TTO data sets (see text). Uncertainties are given for fCO_2 calculated from measured concentrations (TCO_2, TA, TP, TSi, and TB as derived from salinity) using a chemistry model (method $\mathcal{M}_{DIC}$; cross) and from mole fraction measurements (method $\mathcal{M}_{xCO_2}$) taken at air equilibrated with the sample at in situ temperature, SST, (filled triangle), at 4 °C (open triangle) and at 20 °C (diamond). The thin solid lines are smoothing polynomials through the data points.