

Comparison of discrete and underway CO₂ measurements: Inferences on the temperature dependence of the fugacity of CO₂ in seawater

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Abstract

The fugacity or partial pressure of CO₂ in surface water (fCO_{2w}) is a key parameter to determine air-sea CO₂ fluxes and the evolution of ocean acidification. Despite its importance some key physical chemical characteristics are not fully resolved, notably its dependence on temperature. The fCO_{2w} is mostly measured by autonomous underway systems near *in situ* sea surface temperature (SST). Subsurface measurements are commonly carried out on individual (discrete) samples at a fixed temperature, normally 20°C. Here, the underway system observations are compared with co-located discrete observations to determine the consistency of these types of measurements. The co-located discrete fCO_{2w} at 20°C and underway fCO_{2w} measurements at SST are used to infer the temperature dependence of CO₂. In addition, calculated fCO_{2w} from total alkalinity (TA) and total dissolved inorganic carbon (DIC) are compared with the underway and discrete fCO_{2w} measurements. For 21 cruises spanning the major ocean basins from 1992-2020 a temperature dependence of $4.13 \pm 0.01\% \text{ } ^\circ\text{C}^{-1}$ is determined in close agreement with a widely used previous empirical of $4.23 \pm 0.02\% \text{ } ^\circ\text{C}^{-1}$ for North Atlantic surface water. The temperature dependency of calculated fCO_{2w} from TA and DIC using recommended constants is $4.10\% \text{ } ^\circ\text{C}^{-1}$ for 17 cruises where there are co-located measurements of fCO_{2w}, TA and DIC.

Keywords: chemical oceanography, carbon system, carbon dioxide, thermodynamics

Introduction

The fugacity of CO₂, which is the partial pressure of CO₂ corrected for non-ideality, in seawater (fCO_{2w}) is a fundamental quantity to determine air-sea CO₂ fluxes and it is measured extensively throughout the world's oceans. The high-quality measurements are largely performed with flow-through equilibrators where headspace equilibrated with surface seawater are analyzed (Pierrot et al., 2009). Systems are automated and over 30 million samples from ships of opportunity (SOOP) have been measured and collated to date (Bakker et al., 2016; Takahashi et al., 2020). Most of the surface water fCO_{2w} measurements are performed near *in situ* temperature and adjusted to sea surface temperature (SST) utilizing an empirical temperature correction of $4.23\% \text{ } ^\circ\text{C}^{-1}$ based on a laboratory experiment with a single seawater aliquot (Takahashi et al., 1993). However, this dependency differs from theoretical estimates both in magnitude and its invariance with inorganic carbon chemistry and temperature.

A smaller number of discrete $f\text{CO}_{2w}$ measurements have been obtained by taking seawater aliquots of fixed volume and equilibrating the water with a small headspace, and subsequent analysis of the headspace. These analyses are performed at a fixed temperature, usually 20°C . An important application of discrete sub-surface $f\text{CO}_{2w}$ analyses is to assess the internal consistency of the inorganic carbon system in seawater. Because of its sensitivity, it can be used effectively with other inorganic carbon parameters, notably dissolved inorganic carbon (DIC) or total alkalinity (TA) to calculate TA, DIC, pH and other inorganic carbon parameters (Garcia-Ibanez et al., 2022).

The fugacity of CO_2 in surface and subsurface waters has also been derived from pH measurements from profiling floats (Bushinsky et al., 2019; Gray et al., 2018). The intrinsic value of $f\text{CO}_{2w}$ information derived from pH is to determine air-sea CO_2 fluxes and outgassing potential referred to as potential $f\text{CO}_2$ anomaly. This application has recently been highlighted by Chen et al. (2019). Validation of calculated $f\text{CO}_{2w}$ using discrete $f\text{CO}_{2w}$ measurements is critical for such applications as it avoids errors and biases when converting pH to $f\text{CO}_{2w}$. For this application its temperature dependence must be known in order to convert the measured $f\text{CO}_{2w}$ to *in situ* conditions.

Most applications, whether surface $f\text{CO}_{2w}$ measurements or subsurface $f\text{CO}_{2w}$ measurements, require a temperature adjustment. There are two ways to do so: (1) the correction can be performed by utilizing software packages to determine inorganic carbon speciation in seawater (Lewis and Wallace, 1998; Pierrot et al., 2006) if a second inorganic carbon system parameter is known; or (2) by empirical dependencies based on theory, field, and laboratory studies (Copin-Montegut, 1988; Gordon and Jones, 1973; Goyet et al., 1993; Takahashi et al., 1993; Weiss et al., 1982). In general, for small corrections ($\Delta T \approx <1^\circ\text{C}$) empirical estimates are used while for larger temperature adjustments thermodynamic equations are preferred if TA and/or DIC are available. However, the thermodynamic equations can yield significantly different dependencies depending on the dissociation constants used. Of the empirical estimates, the one proposed by Takahashi et al. (1993) that assumes constant temperature dependence, irrespective of seawater composition, is most frequently applied. The equations of Weiss et al. (1982), Copin-Montegut (1988), and Gordon and Jones (1973) include temperature, salinity, and/or $f\text{CO}_{2w}$ as predictor variables, and were derived from fitting results of calculated $f\text{CO}_{2w}$ with varying seawater carbonate compositions. Goyet et al. (1993) developed a 25-parameter fit

algorithm of $f\text{CO}_{2w}$ dependence based on the carbonate dissociation constants of Goyet and Poisson (1989) that includes a dependence on temperature and on inorganic carbon composition in form of the ratio of TA and DIC.

The data used to derive the empirical temperature dependence of Takahashi et al. (1993) is detailed in the appendix of their paper. It is based on a laboratory study using an aliquot of North Atlantic surface water and measurements of the partial pressure of CO_2 of a 500-ml aliquot, or discrete $p\text{CO}_2$, at 8 different temperatures ranging from 2.1 to 24.5°C. The data were fitted as $\partial\ln(p\text{CO}_2)/\partial T$ yielding a dependence of $0.0423 \pm 0.0002 \text{ }^\circ\text{C}^{-1}$ with a standard error (SE) of $\pm 1 \text{ } \mu\text{atm}$, or a temperature dependence $\partial\ln(p\text{CO}_2)/\partial T = 0.0433 - 8.7 \cdot 10^{-5} T$ with a similar SE, where T is in °C (Takahashi et al., 1993; 2009). The latter temperature dependent formulation yields a $\partial\ln(p\text{CO}_2)/\partial T$ value of 0.0431 at 2°C; 0.0416 at 20°C; and 0.0407 at 30°C.

Here, the temperature dependence of $f\text{CO}_{2w}$ in surface water is determined from extensive compilations of co-located measurements of underway $f\text{CO}_{2w}$ and discrete $f\text{CO}_{2w}$ on research cruises spanning all major ocean basins and covering a time period from 1991-2020 (Figure 1). All data used underwent quality control and only data flagged as “good” (WOCE/WHP QC flag = 2) were used. The overall motivation is to assess if a simple temperature dependency can be used over the wide range of environmental conditions encountered during the cruises. As part of the study the quality of the $f\text{CO}_{2w}$ data are investigated with a focus on possible biases over time due to changing instrumentation that are described in supplement S1 and Table S1. This is done by comparison of the discrete $f\text{CO}_{2w}$, underway $f\text{CO}_{2w}$, and $f\text{CO}_{2w}$ calculated from DIC and TA. This work addresses the following aspects:

- Determination of the temperature dependence from comparison of co-located underway measurements at sea surface temperature (SST) and discrete measurements at 20°C.
- Factors influencing the temperature dependence.
- Comparison of calculated $f\text{CO}_{2w}$ from DIC and TA with discrete and underway $f\text{CO}_2$ data.
- A supplement describing the underway CO_2 systems and discrete CO_2 systems used in the study, and possible sources of analytical bias.

The following nomenclature is used: underway surface $f\text{CO}_2$ measurements at sea surface temperature, SST, are referred to as $\text{UW_}f\text{CO}_2$; discrete sample measurements carried at 20°C are listed as $\text{disc_}f\text{CO}_2(20)$; while calculated $f\text{CO}_{2w}$ from DIC and TA are referred to as $f\text{CO}_2(20)(\text{DIC,TA})$, or $f\text{CO}_2(\text{SST})(\text{DIC,TA})$ if the calculation is performed at 20°C or at *in situ* sea surface temperature, respectively. Fugacity differs slightly from partial pressure of CO_2 as it takes into account the molecular interactions between air and CO_2 that cause the gas to behave in a non-ideal way. The two parameters are numerically similar with $f\text{CO}_2 \approx 0.997 \text{ pCO}_2$, or $f\text{CO}_2$ being about $1.2 \mu\text{atm}$ lower than pCO_2 for $f\text{CO}_2(20)$ levels of $\approx 400 \mu\text{atm}$. The differences in temperature dependence of $f\text{CO}_{2w}$ compared to pCO_{2w} are negligible at $\approx 0.01\%$. We therefore do not convert pCO_2 to $f\text{CO}_2$ if the temperature dependencies determined in previous studies by other investigators are expressed in terms of pCO_{2w} when used in our comparisons.

For 17 of the 21 cruises, co-located surface DIC and TA are available and they are used to calculate $f\text{CO}_2(\text{DIC,TA})$ as an independent assessment of $f\text{CO}_{2w}$, recognizing the overall uncertainties in the calculated $f\text{CO}_{2w}$ (see Ellison and Williams, 2012 for the terminology for uncertainty). For the earlier cruises, the overall uncertainty in calculated $f\text{CO}_2(20)$ is $\approx 6 \mu\text{atm}$ (Millero, 1995) based on the propagation of analytical uncertainty in the measurement of DIC of $2 \mu\text{mol kg}^{-1}$ and TA of $4 \mu\text{mol kg}^{-1}$. The standard uncertainties in dissociation constants are not included in the estimate and can lead to biases of $10 \mu\text{atm}$ (Millero et al., 1995). The TA measurements have improved over time and are now good to within $2\text{-}3 \mu\text{mol kg}^{-1}$. A standard uncertainty in calculated $f\text{CO}_2(20)$ surface water is $\approx 4 \mu\text{atm}$ for cruises after reference materials for alkalinity were widely adopted after circa 1995 (Dickson et al., 2003). For the calculations the CO2SsysV2.2 software program (Pierrot et al., 2006) were used with the recommended temperature and salinity dependencies of the dissociation constants (Dickson et al., 2007). The first and second dissociation constants of carbonic acid (K_1 , K_2) are from Lueker et al. (2000); the total boron-salinity relationship is from Uppström (1974); and the sulfate dissociation constants are from Dickson (1990).

Of note is that the more recent determination of the borate-salinity ratio of Lee et al. (2010) will yield a higher borate alkalinity and thus a lower carbonate alkalinity for a given salinity. As a result, surface water $f\text{CO}_2(20)(\text{DIC,TA})$ values are $\approx 6 \mu\text{atm}$ greater using Lee et al. (2010) than when using boron-salinity ratio of Uppström (1974). We show below that the borate-salinity relationship of Uppström yields better agreement between calculated and measured

fCO_{2w} than the higher quality measurements of Lee et al. (2010). The reason is unclear but it could be related to challenges in fully characterizing alkalinity, and, in particular, quantifying the organic alkalinity contribution to total alkalinity (Fong and Dickson, 2019).

All fCO₂(20) data and co-located UW_fCO₂ data used in this study are from investigators at the Atlantic Oceanographic and Meteorological Laboratory of NOAA. The discrete fCO₂ measurements of other investigators often have insufficient metadata that makes it challenging to determine analytical techniques, quality, and data reduction procedures of the, mostly older, discrete measurements. An exception is the observations from the group of Takahashi of the Lamont-Doherty Earth Observatory (LDEO) who made extensive discrete pCO_{2w} measurements but these cruises do not have co-located underway pCO_{2w} measurements. An added issue in tracking down co-located underway CO₂ and discrete CO₂ data is that they are submitted to different depositories and assembling and co-locating the data and metadata for comparison is a challenge.

Methodology to determine the temperature dependence

The temperature dependence of fCO_{2w} was determined by comparing discrete fCO_{2w} measurements at 20°C with co-located underway fCO_{2w} measurements with SST ranging from 1°C to 31°C. This is a uniquely different approach from the common method of determining the dependence either by basing it on thermodynamic constants or by experimentally measuring the fCO_{2w} of a seawater aliquot at different temperatures in the laboratory. As such there is no control of environmental factors that could impact the dependence such as temperature range, fCO_{2w} level, or buffering capacity. The study addresses the universality of the fCO_{2w}-temperature relationship in the field that is commonly assumed in correcting surface water fCO_{2w} levels to a common temperature.

Co-location is not exact and therefore the same water was not sampled, and some of the error is attributed this. The difference in time and location between underway and discrete samples depended on cruise and dataset but maximum differences were 1-hour and 50 km, with later datasets having better co-location due to higher frequency of sampling by the underway systems. The average and standard deviation of the co-location were 1.6 minutes and 8 minutes for time; and 1.4 km and 7 km for distance, respectively. For the older underway systems, the

locations were not logged onto the computer when samples were taken and merging was done after the fact using time of measurement as logged by the data acquisition computer, and the ship supplied location and time information which sometimes were inconsistent. For many comparisons the samples were taken when the ship was stopped on station with the underway system sampling the scientific supply seawater line with bow intake at 3-5 m, and discrete surface samples taken from a CTD-Rosette system at 3-6 m depth such that, whereas not the same water was analyzed, its characteristics were similar based on comparison of salinities. On a few cruises, the comparison was between disc_fCO₂(20) samples taken from the same scientific supply seawater line as used for the equilibrator of the underway CO₂ system (Table 1). These samples were generally obtained while the ship was moving and assurance of sampling the same water is again not possible due to response and lag times of the underway systems such that some variability, but no large systematic differences, in water composition are expected. No significant differences between results of the different sampling approaches were observed. For the A13.5- 2020_truncated cruise, a comparison of using a single underway or an average of 6 underway values bracketing the discrete sampling time yielded an insignificant difference of $-0.05 \pm 0.78 \mu\text{atm}$ (n=175). For co-locating samples at CTD-Rosette stations, an underway analysis taken towards the end of the cast is used, as this is when the discrete sample near the surface is taken. Sampling different waters is believed to cause random variability.

The underway fCO_{2w} measurements are made with an air-water equilibrator situated in the research ship's laboratory at a temperature generally slightly above SST due to warming of water inside the ship (See Supplement 1). The underway fCO₂ data is adjusted for the temperature difference of ($\approx 0.1-0.2^\circ\text{C}$) between equilibrator and SST using a $4.23\% \text{ }^\circ\text{C}^{-1}$ temperature adjustment (Pierrot et al., 2009). This amounts to $3.5 \mu\text{atm}$ for a UW_fCO₂ of $420 \mu\text{atm}$ and a temperature difference of 0.2°C . The temperature difference between UW_fCO₂ and disc_fCO₂(20) is generally much greater, and the applied correction of $4.23\% \text{ }^\circ\text{C}^{-1}$ to determine the UW_fCO₂ at SST is very similar to the final result of $4.13\% \text{ }^\circ\text{C}^{-1}$, such that this adjustment has no discernable impact on the calculated temperature dependence.

The temperature dependence for each cruise was determined by assuming either a constant dependency of the natural logarithm of fCO_{2w}, $\ln(\text{fCO}_{2w})$ with temperature (T), or a linear dependence of $\ln(\text{fCO}_{2w})$ with temperature, or, in equation form:

$$\partial \ln(f\text{CO}_{2w}) / \partial T^{-1} = A_0 \quad (1)$$

and

$$\partial \ln(f\text{CO}_{2w}) / \partial T^{-1} = B_0 + B_1 T \quad (2)$$

Upon integration of (1) and (2), these yield:

$$f\text{CO}_{2w,T2} = f\text{CO}_{2w,T1} \exp(A_0 (T_2 - T_1)) \quad (3)$$

and

$$f\text{CO}_{2w,T2} = f\text{CO}_{2w,T1} \exp[(B_0 (T_2 - T_1) + 0.5 B_1 (T_2^2 - T_1^2))] \quad (4)$$

For our work, T_1 is 20°C and T_2 is SST; A_0 is the constant temperature dependence (°C⁻¹); B_0 is the temperature constant; and B_1 is the temperature coefficient of $\partial \ln(f\text{CO}_{2w}) / \partial T^{-1}$.

For each cruise, $\ln(\text{UW_fCO}_2/\text{disc_fCO}_2(20))$ was regressed against (SST-20) where the slope of the regression provides the temperature dependence, and the intercept is the natural logarithm of the ratio between underway and discrete measurements at 20°C. The regression and intercept were determined for each cruise (Table 1). For further analyses, all data were subsequently merged and a regression of all data was performed. Values two standard deviations (0.058) from this linear trend line of $\ln(\text{UW_fCO}_2/\text{disc_fCO}_2(20))$ versus (SST-20) were omitted from analysis which decreased the total number of data points used from 2223 to 2071. This corresponded to omitting between zero to four data points per cruise, except for SATl91_L1_L2, P18-94_CGC94, and GOMECC2(Sta) where 7, 7, and 16 data points, respectively, were omitted (Table 1). For the older cruises it is likely collocation issues as the original underway pCO₂ systems did not capture GPS data (Table S1). For the coastal cruise GOMECC2(Sta), where 11% of the collocated data were not used, we hypothesize that near-surface stratification between intake and Niskin trip depth caused the outliers. After deleting the points, data from each cruise was regressed again and presented in Table 1 and Figure 2. The overall trend of the entire datasets did not change by removing outliers but goodness of fit with a standard error of 0.016, of course, improved.

The $f\text{CO}_{2w}$ calculated from DIC and TA, $f\text{CO}_2(20)(\text{DIC,TA})$ and $f\text{CO}_2(\text{SST})(\text{DIC,TA})$ were used to determine the temperature dependence in a similar fashion as with the measured

values for the conditions under which samples were taken (Table 2). This provides an indication how well the observation-based empirical temperature dependence compared with the temperature dependence of the calculated values, and thus is an indication of whether the temperature dependence of the carbonate dissociation constants determined in laboratory settings match “real world” conditions.

Results

The surface water data over 3 decades are analyzed to determine the dependency of $f\text{CO}_{2w}$ on temperature and carbonate speciation. A summary of results for the 21 cruises are provided in Table 1. The tabulation provides the intercept, the slope and standard error (SE) of $\ln(\text{UW_fCO}_2/\text{disc_fCO}_2(20))$ versus $(\text{SST}-20)$, where SST is the sea surface temperature determined at the ship’s intake. If a functionality of $\partial\ln(f\text{CO}_{2w})/\partial T$ is assumed then the slope of the relationship $\ln(f\text{CO}_2)$ versus temperature is the temperature dependence. The quantities in Table 1 are multiplied by 100, to provide the often-used expression of percent per degree ($\% \text{ } ^\circ\text{C}^{-1}$). The constant temperature dependence ranges from $3.76\% \text{ } ^\circ\text{C}^{-1}$ for the 1998 GasEx cruise in the North Atlantic to $4.51\% \text{ } ^\circ\text{C}^{-1}$ for a cruise in the Equatorial Pacific in 1992 (EqPac Spring-92). The average and SE of the slopes for each of the 21 cruises is $4.09\pm 0.19\% \text{ } ^\circ\text{C}^{-1}$ which is in agreement with the regression for all data of $4.13\pm 0.01\% \text{ } ^\circ\text{C}^{-1}$.

The intercept of $\ln(\text{UW_fCO}_2/\text{disc_fCO}_2(20))$ versus $\text{SST}-20 \text{ } ^\circ\text{C}$ provided in Table 1 is the bias between $\ln(\text{UW_fCO}_2)$ and $\ln(\text{disc_fCO}_2(20))$ at 20°C . Thus, $e^{(\text{Intercept})}$ provides the ratio between UW_fCO_{2w} and $\text{disc_fCO}_2(20)$ at 20°C . The ratio between $\text{UW_fCO}_2(20)$ and $\text{disc_fCO}_2(20)$ ranges from $\text{UW_fCO}_2(20) = 0.954 \text{ disc_fCO}_2(20)$ for the EqPac Spring-92 cruise to $\text{UW_fCO}_2(20) = 1.023 \text{ disc_fCO}_2(20)$ for the coastal GOMECC-3 cruise in 2017. For all cruises, the average of the ratio of $\text{disc_fCO}_2(20)$ to UW_fCO_2 at $20 \text{ } ^\circ\text{C}$ is 0.992 ± 0.017 . For a $f\text{CO}_{2w}$ of $400 \text{ } \mu\text{atm}$ this translates to an offset of $-3.2 \text{ } \mu\text{atm}$ with a standard deviation of $6.8 \text{ } \mu\text{atm}$, with disc_fCO_2 being greater. These average offset and standard deviation are slightly greater than expected from analytical accuracy with are better than 1% for discrete measurements and $2 \text{ } \mu\text{atm}$ for underway measurements. For several cruises, when SSTs for the whole cruise were far greater than 20°C , the intercept at 20°C is extrapolated down to 20°C .

Some cruises show biases and analytical uncertainties in measurements that are greater than inferred from replicate samples. Possible offsets of data from older instrumentation (Table S1) prior to 2000 were possibly caused by incomplete equilibration due to ambient air entering the equilibration chamber of the underway systems, and loss of headspace in the discrete systems (Wanninkhof and Thoning, 1993). These issues would be most apparent at high and low $f\text{CO}_{2w}$ levels and cause a bias towards ambient air CO_2 levels. We surmise both of these issues could be at play for the EqPac Spring-92 and EqPac Fall-92 studies where the high CO_2 levels of the Equatorial Pacific measured by the underway systems might be biased low which could explain both the negative intercept and high slope for these studies. Except for these cases, there is no clear dependency on time, location, instrument used, temperature range, or chemical composition to explain the small differences between $\text{disc_fCO}_2(20)$ and underway measurements interpolated to 20°C , or the slope of the temperature dependency for each of the cruises. We attribute cruise to cruise differences largely to sampling mismatch between underway and discrete observations and analytical uncertainties including differences in instrument performance.

The number of observations and temperature range of data for each cruise are limited, and individual cruise results show similar scatter in datapoints. Therefore, the dataset is investigated as a single entity. The collated data regressed as $\ln(\text{UW_fCO}_2/\text{disc_fCO}_2(20))$ against $(\text{SST}-20)$ provide the temperature dependence of $f\text{CO}_{2w}$ and are used to address the question of whether the temperature dependence is a function of temperature and carbonate chemistry as the internal consistency calculations suggest. Two fits are performed for the relationship of $\ln(\text{UW_fCO}_2/\text{disc_fCO}_2(20))$ versus $(\text{SST}-20)$ (Eqns. 1 and 2). A linear fit yields a slope of 0.0413, and a coefficient of determination, r^2 , of 0.996 ($n=2071$), while a fit with temperature shows a weak functionality with temperature of $\partial\ln(f\text{CO}_{2w})/\partial T = 0.0413 - 2.19 \cdot 10^{-5} \text{ SST}$, $r^2 = 0.996$ ($n=2071$) (Figure 2). Of note is that the 2nd order fit yields slightly lower values at higher temperatures with a temperature dependence of $0.0413^\circ\text{C}^{-1}$ at 0°C , and $0.0405^\circ\text{C}^{-1}$ at 30°C . A F-test is performed on the significance of the temperature dependent term, $2.19 \cdot 10^{-5} \text{ SST}$, based on differences in the standard error of the constant and temperature dependent fits. A F-value of 1.004 was obtained, and compared to the lookup table value of 1.352, indicates that the temperature dependent term is not significant for this dataset.

To assess the consistency of the $f\text{CO}_{2w}$ data and to further evaluate factors that influence the $f\text{CO}_{2w}$ temperature dependence, the $f\text{CO}_{2w}$ data were compared with $f\text{CO}_{2w}$ calculated from co-located DIC and TA samples that were available for about 80% of the co-located UW_fCO_2 and $\text{disc}_f\text{CO}_2(20)$ samples. The calculated $f\text{CO}_2(\text{TA},\text{DIC})$ is dependent on the carbonate dissociation and other seawater thermodynamic constants used. Here, we use the widely accepted dependency of the dissociations constants on temperature and salinity listed in the introduction. As noted above the borate salinity ratio of Lee et al. (2010) yields poorer correspondence between measured and calculated parameters than those of Uppström (1974). The average difference for all data between $\text{disc}_f\text{CO}_2(20)-f\text{CO}_2(20)(\text{TA},\text{DIC})$ using Lee et al. (2010) is $-6.2 \pm 6.9 \mu\text{atm}$ ($n=1788$), compared to $\text{disc}_f\text{CO}_2(20)-f\text{CO}_2(20)(\text{TA},\text{DIC})$ of $-1.3 \pm 6.8 \mu\text{atm}$ ($n=1788$) using the Uppström boron-salinity relationship.

The comparison of calculated versus measured $f\text{CO}_{2w}$ for each cruise is summarized in Table 2. The agreement between $\text{disc}_f\text{CO}_2(20)$ and $f\text{CO}_2(20)(\text{TA},\text{DIC})$ for the full dataset is $-1.3 \pm 6.8 \mu\text{atm}$ ($n=1788$), and for $\text{UW}_f\text{CO}_2(\text{SST})$ and $f\text{CO}_2(\text{SST})(\text{TA},\text{DIC})$ it is $-2.9 \pm 9.2 \mu\text{atm}$ ($n=1617$). The smaller standard uncertainty in the $\text{disc}_f\text{CO}_2(20)$ and $f\text{CO}_2(20)(\text{TA},\text{DIC})$ comparison is attributed to the TA and DIC samples being taken from the same Niskin bottle as the $\text{disc}_f\text{CO}_2(20)$ samples. The cruise-to-cruise differences were not significant based on their standard uncertainty (Table 2). The temperature dependence of $f\text{CO}_2(\text{TA},\text{DIC})$ determined from $\partial \ln(f\text{CO}_2(\text{SST})(\text{TA},\text{DIC})/f\text{CO}_2(20)(\text{TA},\text{DIC}))$ versus $(\text{SST}-20)$ for all the quality-controlled data used is $0.0410 \text{ }^\circ\text{C}^{-1}$, or $(0.0412 - 6.56 \cdot 10^{-5} \text{ SST}) \text{ }^\circ\text{C}^{-1}$, where the temperature dependence is not significant based on an F-test.

With few exceptions, for individual cruises there is good agreement between $f\text{CO}_{2w}$ and $f\text{CO}_2(\text{TA},\text{DIC})$ for both the underway and discrete samples. The A13.5_2020_trunc cruise data show a difference between $\text{UW}_f\text{CO}_2(\text{SST})$ and $f\text{CO}_2(\text{SST})(\text{TA},\text{DIC})$ of $-9.04 \pm 3.88 \mu\text{atm}$ ($n=220$) and a difference of $-7.88 \pm 4.70 \mu\text{atm}$ ($n=225$) between $\text{disc}_f\text{CO}_2(20)$ and $f\text{CO}_2(20)(\text{TA},\text{DIC})$ measurements. As the average differences between measured and calculated discrete and underway $f\text{CO}_{2w}$ are similar, a bias in either DIC or TA is probable for this cruise. The P18-94_CGC94 cruise shows a large difference and standard uncertainty in $\text{UW}_f\text{CO}_2(\text{SST})$ and $f\text{CO}_2(\text{SST})(\text{TA},\text{DIC})$ of $-8.38 \pm 9.02 \mu\text{atm}$ ($n=76$), but not in $\text{disc}_f\text{CO}_2(20)$ and $f\text{CO}_2(20)(\text{TA},\text{DIC})$ with a difference of $-1.33 \pm 6.79 \mu\text{atm}$ ($n=132$). This is attributed to the underway CO_2 system on that cruise trending towards ambient CO_2 values at high and low

$f\text{CO}_{2w}$ due to laboratory air entering the equilibrator through the vents (Wanninkhof and Thoning 1993). This could also be the cause of a lower temperature dependence, $\partial \ln(f\text{CO}_{2w})/\partial T$, of $3.82\% \text{ } ^\circ\text{C}^{-1}$ for this cruise (See Table 1).

Discussion

For the interpretation of the temperature dependence and factors influencing this dependence the full quality-controlled dataset is used, along with theoretical dependencies and other empirical relationships that appear in the literature. As listed in the results, some cruises show slight biases but the attribution is not definitive, such that all cruises are retained for the discussion.

Thermodynamic foundation of the temperature dependency of $f\text{CO}_{2w}$

The temperature dependence of $f\text{CO}_{2w}$ is a combination of a temperature dependence of the solubility of CO_2 in seawater (Eqn. 5), and the temperature and salinity dependence of carbonate dissociation constants (Eqns. 6, 7) as seen from the following chemical equations:

$$f\text{CO}_{2w} = [\text{CO}_2]_{\text{aq}}/K_0 \quad (5)$$

$$[\text{CO}_2]_{\text{aq}} = [\text{H}^+] [\text{HCO}_3^-]/K_1 \quad (6)$$

$$[\text{HCO}_3^-] = [\text{H}^+] [\text{CO}_3^{2-}]/K_2 \quad (7)$$

where $[\text{CO}_2]_{\text{aq}}$ is the concentration of undissociated CO_2 in seawater, $[\text{H}^+]$ is the hydrogen ion concentration; $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ are the concentrations of bicarbonate and carbonate ion, respectively; K_0 is the solubility constant of CO_2 in seawater; and K_1 and K_2 are the first and second stoichiometric carbonate dissociation constants, respectively. Increasing temperatures will decrease K_0 , K_1 , and K_2 and thereby increasing $f\text{CO}_{2w}$ at constant DIC and TA. The temperature dependence of K_0 and the combined temperature dependence of K_1 and K_2 , each contribute about half of the total observed temperature dependency of $f\text{CO}_{2w}$ in seawater of $\approx 4\% \text{ } ^\circ\text{C}^{-1}$. Thus, the temperature dependence of the buffered seawater carbonate system is about twice that of most other slightly soluble gases (Wilhelm et al., 1977). As can be discerned from equations 6 and 7, the magnitude of $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ will have an influence on $f\text{CO}_{2w}$ and thus its temperature dependency. In other words, the inorganic carbon composition and

speciation of seawater should impact the dependency which is not implicitly included in the temperature dependency as derived here. This dependency on inorganic carbon speciation has been expressed in terms of TA/DIC (Goyet et al., 1993). The TA/DIC is decreasing over time due to invasion of anthropogenic CO₂ such that the temperature dependency of fCO_{2w} should decrease as well.

Previous studies on temperature dependency of fCO_{2w}

Some of the earliest studies addressing the temperature dependence of fCO_{2w} and resulting empirical equations are from Gordon and Jones (1973) and Weiss et al. (1982). Gordon and Jones (1973) calculated pCO_{2w} for a range of salinity (28-36), TA (1800-2400 μmol kg⁻¹), and pH (7.5-8.6) values. They used carbonate dissociation constants from Lyman (1956) to calculate pCO₂. The resulting temperature dependence expressed as a function of pCO₂ was: $\partial pCO_2/\partial T = 4.4 \cdot 10^{-2} pCO_{2w} - 4.6 \cdot 10^{-6} (pCO_{2w})^2$. Weiss et al. (1982) performed a similar exercise that was guided by results from surface water observations of T, S, fCO₂ and TA from the NORPAX Equatorial Pacific experiment in 1979 and 1980. They used carbonate dissociation constants from Hansson (1973). A fit of $\partial \ln(fCO_{2w})/\partial T = 0.03107 - 2.785 \cdot 10^{-4} T - 1.839 \cdot 10^{-3} \ln(fCO_{2w})$ was obtained. Note, in this equation the fCO_{2w} predictor on the right hand appears to be expressed in atm rather than μatm. The relationship, along with our results and those of Takahashi et al. (1993) are plotted as $\partial \ln(fCO_{2w})/\partial T$ versus T in Figure 3. For the Gordon and Jones (1973), as well as the Weiss et al. (1982) relationships in Figure 3, a fCO₂(20) = 400 μatm is used, and fCO₂(T) = fCO₂(20) exp(0.0423 (T-20)) for the predictor variable such that the $\partial \ln(fCO_{2w})/\partial T$ is constrained to some extent by an assumed 4.23% °C⁻¹ dependency. Since the derivation of Weiss et al. (1982) includes temperature in addition to $\partial \ln(fCO_{2w})$ as a predictor variable it is less constrained by the assumed dependency of $\ln(fCO_{2w})$. As a result, the $\partial(\ln fCO_{2w})/\partial T$ determined from the Weiss et al. relationship shows a stronger temperature dependency than that of Gordon and Jones (1973). The estimate by Takahashi et al. (1993) based on a laboratory study using North Atlantic Surface water is commonly expressed by a constant T dependency, $\partial(\ln pCO_{2w})/\partial T = 0.0423$ but is also provided with a temperature dependency: $\partial(\ln pCO_{2w})/\partial T = 0.0433 - 8.7 \cdot 10^{-5} T$ (Takahashi et al., 2009) (Figure 3). As noted, the results of our study based on comparing underway and discrete measurement corresponds well to the relationships of Takahashi et al. (1993, 2009) when using a constant temperature dependency but

show a weaker, non-significant, dependency with temperature if expressed as a fit $\partial(\ln f\text{CO}_{2w})/\partial T = (0.0412 - 2.185 \cdot 10^{-5} T)$.

The impact of the TA/DIC on temperature dependency of $f\text{CO}_{2w}$

The temperature dependence of the calculated $f\text{CO}_{2w}$ values from TA and DIC, $\partial(\ln(f\text{CO}_2(\text{TA},\text{DIC}))/\partial T$ for the cruises ranges from 4.06 to 4.29% °C⁻¹ (Table 2). It reflects the small effect that the DIC/TA and SST have on the temperature dependence for the dissociation constants used for this dataset. That is, as the $f\text{CO}_{2w}$ values are determined from TA and DIC, the temperature dependencies show the theoretical dependence of the samples at the measured TA, DIC, sea surface salinity (SSS), and SST. The good agreement of the average of $\partial(\ln(f\text{CO}_2(\text{TA},\text{DIC}))/\partial T$ for the whole dataset of 0.0410 compared to 0.0413 for the measured $\text{disc_}f\text{CO}_2$ and $\text{UW_}f\text{CO}_2$ values indicate consistency between the temperature dependence of calculated and measured values.

The temperature and composition dependency on the $f\text{CO}_{2w}$ temperature relationship, specifically the TA/DIC, was provided by Goyet et al. (1993) with an explicit dependency of $f\text{CO}_{2w}$ on temperature and TA/DIC using a 25-parameter fit with temperature and DIC/TA as predictor variables. The carbonic acid dissociation constants proposed by Goyet and Poisson (1989) were used to generate the fit. The temperature dependence of the relationships of Goyet et al. (1993) of $f\text{CO}_{2w}$ for different TA/DIC are shown in Figure 4. For the comparison, TA/DIC values of 1.05, 1.1, 1.15, and 1.20 are used spanning surface water conditions in the open ocean. The dependent variable in the equation of Goyet et al. (1993), expressed in terms of $\ln(f\text{CO}_{2w}/f\text{CO}_2(20))$, is directly comparable to our analyses. The $f\text{CO}_{2w}$ calculated from DIC and TA using the constants of Lueker et al. (2000) at SSS of 35 are shown in Figure 4 as well. In the figure, a fixed TA of 2310 $\mu\text{mol kg}^{-1}$ and DIC values of 2200, 2100, 2008 and 1925 $\mu\text{mol kg}^{-1}$ and a SSS of 35 were used to get the listed TA/DIC. All relationships show a similar behavior with a higher temperature dependence at low temperatures and high TA/DIC. However, as shown in Figure 4, the magnitude and trend differs appreciably. The parameterization using the constants proposed by Goyet et al. (1993) shows a significantly higher and stronger temperature dependency which is attributed to K_2 determined by Goyet and Poisson (1989) having a stronger temperature dependency compared to the constants of Lueker et al. (2000). The temperature dependencies of calculated $f\text{CO}_2(\text{TA},\text{DIC})$ of Lueker et al. (2000) are more in line with the

experimental results of this study and with the empirical relationship of Takahashi that was based on an aliquot of seawater with $S=35.38$; $DIC=2074 \mu\text{mol kg}^{-1}$, and $TA = 2280 \mu\text{mol kg}^{-1}$ yielding a TA/DIC of 1.1.

Effect of changing TA/DIC in the future

The empirical relationships described here are based on 30 years of data and cover a range of temperatures and different seawater chemistry, notably TA/DIC from 1.06 to 1.24 with a mean of 1.15 ± 0.03 ($n= 1798$) (see Figure S1, supplemental material). Over that period, DIC levels increased by $\approx 20 \mu\text{mol kg}^{-1}$ due to the invasion of anthropogenic CO_2 , which would cause the TA/DIC to decrease by $\approx 1\%$. An estimate of maximum impact of changes in the temperature dependence over time due to increasing surface water DIC for this dataset was investigated by adding $20 \mu\text{mol kg}^{-1}$ to all DIC values measured on the cruises listed in Table 1. The results (Figure 5) show that the fixed temperature dependence, $\partial\ln(\text{fCO}_{2\text{w}})/\partial T$, decreased from $0.0412 \text{ }^\circ\text{C}^{-1}$ for $\text{fCO}_2(\text{TA},\text{DIC})$ to $0.0410 \text{ }^\circ\text{C}^{-1}$ for $\text{fCO}_2(\text{TA},\text{DIC}+20)$ (Figure 5). The dependence as a function of temperature yields $(0.0412-6.15 \cdot 10^{-5} T) \text{ }^\circ\text{C}^{-1}$ for $\text{fCO}_2(\text{TA},\text{DIC})$ compared to $(0.0410- 5.45 \cdot 10^{-5} T) \text{ }^\circ\text{C}^{-1}$ for $\text{fCO}_2(\text{TA},\text{DIC}+20)$. The analysis bears out that increases in the DIC of seawater leads to a slightly weaker temperature dependence. It also points out that the dataset used which covers 3 decades could have small systematic differences in the temperature dependence due to anthropogenic CO_2 increases and the resulting change in TA/DIC. However, for the temperature and composition range encountered, the standard uncertainty in the observations is too large to discern these small systematic differences in our data. As surface water DIC and temperature are expected to continue to increase into the foreseeable future, the temperature dependence should undergo small decreases with time.

The near-constant $\partial\ln(\text{fCO}_{2\text{w}})/\partial T$ observational results that cover a wide range of temperatures and TA/DIC values in this study compared to the theoretical dependency on temperature and TA/DIC can be attributed to several factors. There are cruise-to-cruise differences in the dependency attributed to analytical uncertainty in measurements (Table 2) that mask the $\partial\ln(\text{fCO}_{2\text{w}})/\partial T$ dependencies on T and TA/DIC. Most of the measurements were at the higher end of the SST range with 85% of the samples over 20°C , and 60% of the samples having an SST $> 25^\circ\text{C}$ (Figure S3). The theoretical temperature dependence expressed as $\partial\ln(\text{fCO}_{2\text{w}})/\partial T = B_0 + B_1 T$ shows a stronger dependency at lower temperatures, and weaker dependency at low

TA/DIC values (Figure 4). These conditions often go hand-in-hand in the surface ocean. That is, surface waters of the world's oceans have lower temperatures and lower TA/DIC at higher latitudes such that the two factors will oppose each other. This is seen in the dataset where low TA/DIC and low temperature coincide (Figure S1). Thus, in the surface ocean, the stronger temperature dependence at low temperature will be counteracted by a lower temperature dependence at lower TA/DIC. However, quantitative determination of a temperature dependency for different TA/DIC ranges in our dataset did not yield consistent results because of the correlation of SST and TA/DIC, yielding limited unique SST and TA/DIC data, and analytical uncertainties.

Conclusions

The large dataset of co-located underway and discrete $f\text{CO}_{2w}$ data covers all ocean basins but with most data in the Atlantic Ocean. It shows cruise to cruise temperature dependencies, $\partial\ln(f\text{CO}_{2w})/\partial T$, that range from 0.0376 to 0.0451 $^{\circ}\text{C}^{-1}$ with uncertainties and differences that cannot be attributed to time of measurement, temperature, or chemical composition. These differences are assumed to be primarily caused by small analytical biases. Analyzing the combined data for cruises in the form of $\ln(\text{UW_}f\text{CO}_2/\text{disc_}f\text{CO}_2(20))$ versus SST-20 yields a constant temperature dependence of 0.0413 $^{\circ}\text{C}^{-1}$. Calculated $f\text{CO}_{2w}$ values from co-located TA and DIC measurements using recommended constants show a similar dependence. Previously published estimates of temperature dependence show a significant range that can be traced, in part, to using older carbonate dissociation constants that are not widely used anymore. Using the recommended dissociation constants of Lueker et al. (2000), the $f\text{CO}_{2w}$ - temperature relationship shows a weak dependency on temperature and TA/DIC. The TA/DIC is a proxy for the carbonate buffering, with high TA/DIC (better buffering) showing a stronger temperature dependency. The $\partial\ln(f\text{CO}_{2w})/\partial T$ decreases with temperature. Low TA/DIC in surface waters often coincide with low temperature and thus will have opposing impacts on $\partial\ln(f\text{CO}_{2w})/\partial T$ such that using a constant dependency is appropriate for most small temperature adjustments in $f\text{CO}_{2w}$. For surface water temperature corrections of $f\text{CO}_{2w}$ of $\approx <1^{\circ}\text{C}$ a dependency in the range of 0.0413 to 0.0423 as found in this study and determined by Takahashi et al. (1993), respectively, are consistent with the theoretical estimates calculated using the dissociation constants listed, and will yield adequate temperature corrections when additional carbon system

measurements are not available. For accurate, larger temperature corrections, knowledge of the TA/DIC is necessary and determination of the dependency using the carbonate dissociation constants of Lueker et al. (2000) is suggested based on the results of this study.

Data availability

The collated discrete and underway surface $f\text{CO}_{2w}$ data used in this work are available in Excel format at NCEI (NCEI accession 0247018, <https://www.ncei.noaa.gov/data/oceans/ncei/ocads/metadata/0247018.html>)

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References

- Bakker, D.C.E. et al., 2016. A multi-decade record of high-quality $f\text{CO}_2$ data in version 3 of the Surface Ocean CO_2 Atlas (SOCAT). *Earth System Science Data*, 8: 383-413. <http://dx.doi.org/10.5194/essd-8-383-2016>.
- Bushinsky, S.M. et al., 2019. Reassessing Southern Ocean air-sea CO_2 flux estimates with the addition of biogeochemical float observations. *Global Biogeochemical Cycles*, 33(11): 1370-1388. <http://dx.doi.org/10.1029/2019gb006176>.
- Chen, H., Morrison, A.K., Dufour, C.O. and Sarmiento, J.L., 2019. Deciphering patterns and drivers of heat and carbon storage in the Southern Ocean. *Geophysical Research Letters*, 46(6): 3359-3367. <https://doi.org/10.1029/2018GL080961>.
- Chen, H., Wanninkhof, R., Feely, R.A. and Greeley, D., 1995. Measurement of fugacity of carbon dioxide in sub-surface water: an evaluation of a method based on infrared analysis. ERL AOML-85, NOAA/AOML.
- Chipman, D.W., Marra, J. and Takahashi, T., 1993. Primary production at 47°N and 20°W in the North Atlantic Ocean: A comparison between the ^{14}C incubation method and mixed layer carbon budget observations. *Deep-Sea Research II*, 40: 151-169. [https://doi.org/10.1016/0967-0645\(93\)90011-B](https://doi.org/10.1016/0967-0645(93)90011-B).
- Copin-Montegut, C., 1988. A new formula for the effect of temperature on the partial pressure of CO_2 in seawater. *Marine Chemistry*, 25: 29-37.
- Dickson, A.G., 1990. Standard potential of the reaction: $\text{AgCl(s)} + 1/2 \text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4^- in synthetic seawater from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics*, 22: 113-127.
- Dickson, A.G., Afgan, J.D. and Anderson, G.C., 2003. Reference materials for oceanic CO_2 analysis: A method for certification of total alkalinity. *Marine Chemistry*, 80(2): 185-197. 10.1016/S0304-4203(02)00133-0.
- Dickson, A.G., Sabine, C.L. and Christian, J.R., 2007. Guide to best practices for ocean CO_2 measurements. 3. PICES Special Publication 3, 191 pp.
- Ellison, S.L.R. and Williams, A. (Editors), 2012. Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement. www.eurachem.org.
- Feely, R.A. et al., 1998. A new automated underway system for making high precision $p\text{CO}_2$ measurements onboard research ships. *Analytica Chim. Acta*, 377: 185-191.
- Fong, M.B. and Dickson, A.G., 2019. Insights from GO-SHIP hydrography data into the thermodynamic consistency of CO_2 system measurements in seawater. *Marine Chemistry*, 211: 52-63. <https://doi.org/10.1016/j.marchem.2019.03.006>.
- García-Ibáñez, M.I. et al., 2022. Gaining insights into the seawater carbonate system using discrete $f\text{CO}_2$ measurements. *Marine Chemistry*, 245: 104150. <https://doi.org/10.1016/j.marchem.2022.104150>.
- Gordon, L.I. and Jones, L.B., 1973. The effect of temperature on carbon dioxide partial pressures in seawater. *Marine Chemistry*, 1(4): 317-322. [https://doi.org/10.1016/0304-4203\(73\)90021-2](https://doi.org/10.1016/0304-4203(73)90021-2).
- Goyet, C., Millero, F.J., Poisson, A. and Shafer, D.K., 1993. Temperature dependence of CO_2 fugacity in seawater. *Marine Chemistry*, 44(2): 205-219. [https://doi.org/10.1016/0304-4203\(93\)90203-Z](https://doi.org/10.1016/0304-4203(93)90203-Z).
- Goyet, C. and Poisson, A., 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Research*, 36: 1635-1654.

- Gray, A.R. et al., 2018. Autonomous biogeochemical floats detect significant carbon dioxide outgassing in the high-latitude Southern Ocean. *Geophysical Research Letters*, <http://dx.doi.org/10.1029/2018GL078013>.
- Hansson, I., 1973. A new set of acidity constants for carbonic acid and boric acid in seawater. *Deep-Sea Research*, 20: 461-478.
- Ho, D.T., Wanninkhof, R., Masters, J., Feelt, R.A. and Cosca, C.E., 1997. Measurements of underway $f\text{CO}_2$ in the Eastern Equatorial Pacific on NOAA Ships Malcolm Baldrige and Discoverer from February to September 1994. NOAA Data Report ERL-AOML 30 Atlantic Oceanographic and Meteorological Laboratory, Miami, FL.
- Johnson, J.E., 1999. Evaluation of a seawater equilibrators for shipboard analysis of dissolved oceanic trace gases. *Analytica Chimica Acta*, 395: 119.
- Lee, K. et al., 2010. The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta*, 74(6): 1801-1811. <http://dx.doi.org/10.1016/j.gca.2009.12.027>.
- Lewis, E. and Wallace, D.W.R., 1998. Program developed for CO_2 system calculations. ORNL/CDIAC-105, Oak Ridge National Laboratory, Oak Ridge.
- Lueker, T.J., Dickson, A.G. and Keeling, C.D., 2000. Ocean $p\text{CO}_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2 ; validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry*, 70: 105-119.
- Lyman, J., 1956. Buffer mechanism of sea water, Univ. of Calif. Los Angeles.
- Millero, F.J., 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta*, 59: 661-677.
- Neill, C., Johnson, K.M., Lewis, E. and Wallace, D.W.R., 1997. Accurate headspace analysis of $f\text{CO}_2$ in discrete water samples using batch equilibration. *Limnology and Oceanography*, 42(8): 1774-1783.
- Perez, F.F. and Fraga, F., 1987. A precise and rapid analytical procedure for alkalinity determination. *Marine Chemistry*, 21: 169-182.
- Pierrot, D., Lewis, E. and Wallace, D.W.R., 2006. MS Excel program developed for CO_2 system calculations. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a.
- Pierrot, D. et al., 2009. Recommendations for autonomous underway $p\text{CO}_2$ measuring systems and data reduction routines. *Deep -Sea Res II*, 56: 512-522.
- Takahashi, T., Olafsson, J., Goddard, J.G., Chipman, D.W. and Sutherland, S.C., 1993. Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochemical Cycles*, 7: 843-878. <https://doi.org/10.1029/93GB02263>.
- Takahashi, T., Sutherland, S.C. and Kozyr, A., 2020. Global Ocean Surface Water Partial Pressure of CO_2 Database: Measurements Performed During 1957-2019 (LDEO Database Version 2019) (NCEI Accession 0160492). Version 9.9. NOAA National Centers for Environmental Information.
- Tans, P.P., Crotwell, A.M. and Thoning, K.W., 2017. Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements. *Atmospheric Measurement Techniques*, 10: 2669-2685. <https://doi.org/10.5194/amt-10-2669-2017>.

- Uppström, L.R., 1974. The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep-Sea Research*, 21: 161-162. [https://doi.org/10.1016/0011-7471\(74\)90074-6](https://doi.org/10.1016/0011-7471(74)90074-6).
- Wanninkhof, R. and Thoning, K., 1993. Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods. *Marine Chemistry*, 44(2-4): 189-205.
- Weiss, R.F., Jahnke, R.A. and Keeling, C.D., 1982. Seasonal effects of temperature and salinity on the partial pressure of CO₂ in seawater. *Nature*, 300: 511-513.
- Weiss, R.F. and Price, B.A., 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry*, 8: 347-359. [https://doi.org/10.1016/0304-4203\(80\)90024-9](https://doi.org/10.1016/0304-4203(80)90024-9).
- Wilhelm, E., Battino, R. and Wilcock, R.J., 1977. Low pressure solubility of gases in liquid water. *Chemical Reviews*, 77: 219-262.

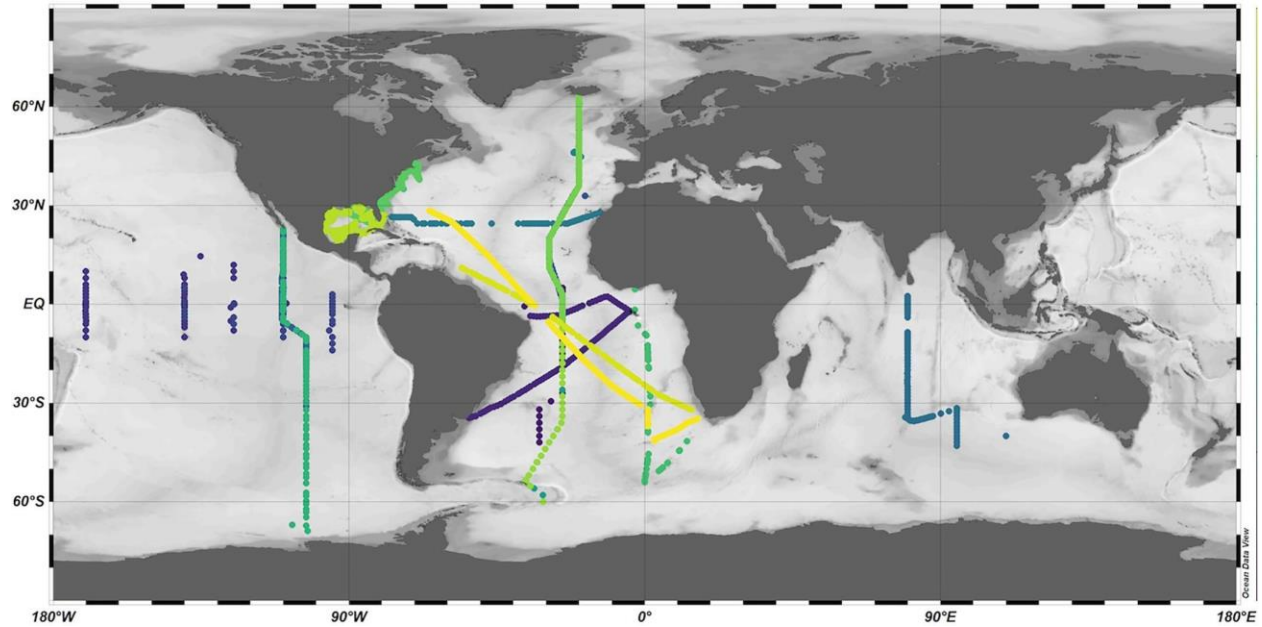


Figure 1. Sample locations for surface disc_fCO₂(20) and UW_fCO₂ samples. Cruise tracks are color coded: SATl91= dark blue; EqPac-Spring92 and EqPac-Fall92= purple; NATl93, SATl91, NATl-2003_A16N , SATl-2005_A16S, A16N_2013, and A16S_2014= overlapping lime green and fern green; P18-94_CGC94, and P18-2008= jade green; IO95_I8N= pine green; A05- 98_24N= pine green; GasEx-98_L2= artichoke green; GOMECC1-2007= sage green; A13.5_2010= emerald green; GOMECC2_2012 and GOMECC3_2017= lime green; A13.5_2020_transit= dark yellow; A13.5_2020_trunc= yellow.

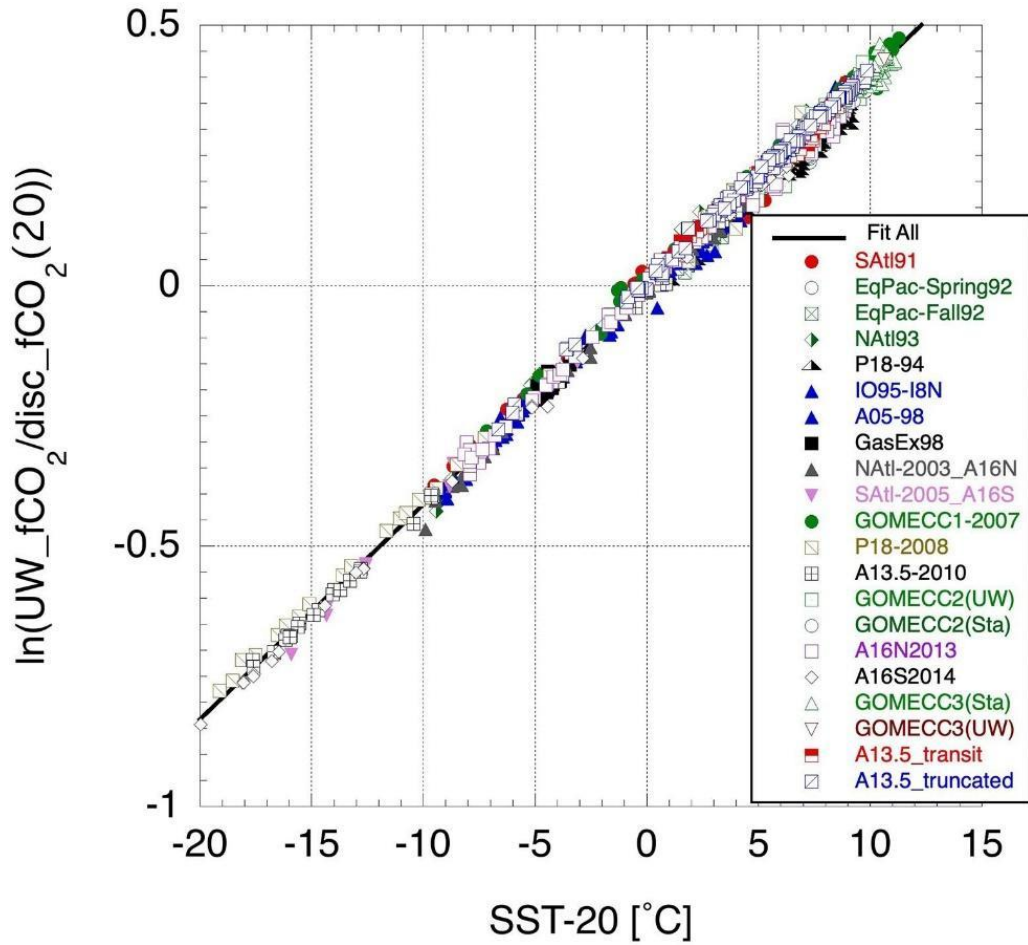


Figure 2. Temperature dependence determined from underway and discrete fCO_{2w} for all cruises studied (Table 1), with cruise abbreviations in the legend. Data are plotted as $\ln(UW_fCO_2/disc_fCO_2(20))$ against (SST-20) where the slope gives the temperature dependence. A linear fit shown by the black line gives a fixed temperature dependence of 0.0413, $r^2=0.996$; whereas a polynomial yields dependence on temperature of $0.0412-2.186 \cdot 10^{-5} T$, $r^2=0.996$.

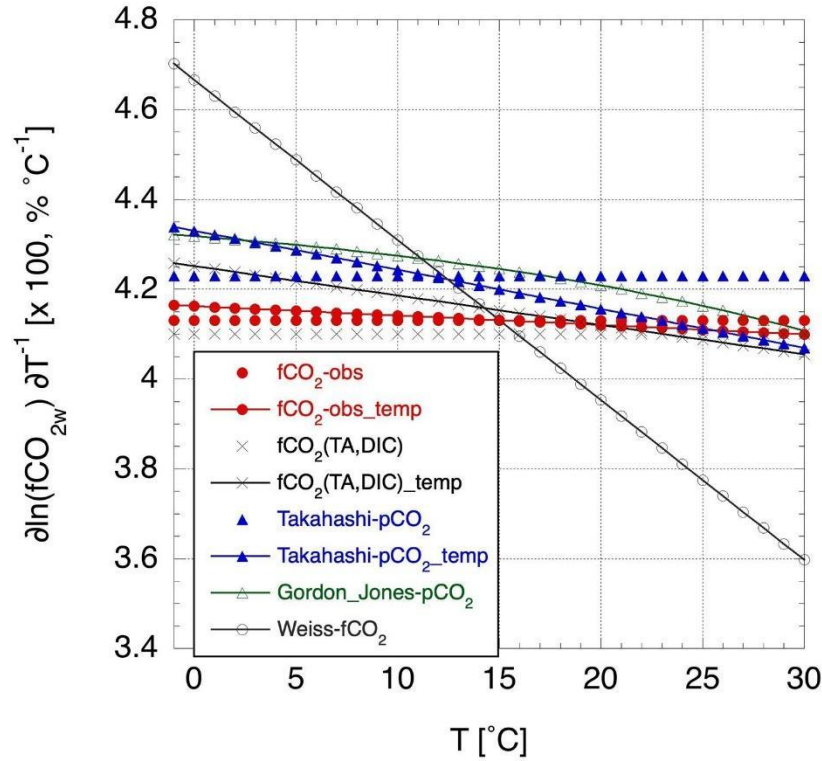


Figure 3. Different temperature dependencies expressed as $\partial \ln(\text{fCO}_{2\text{w}}) / \partial T$ [$\times 100, \% \text{ } ^\circ\text{C}^{-1}$]. The solid red circles and solid red circles with line are the fixed and linear temperature dependencies based on this work; the gray crosses and black line with crosses are the fixed and linear dependencies based on this work using calculated $\text{fCO}_{2\text{w}}$ from TA and DIC; the open circles are those of Weiss et al. (1982) using a $\text{fCO}_2(20)$ of $400 \mu\text{atm}$; the open triangles are the results of Gordon and Jones (1973) also using a $\text{pCO}_{2\text{w}}(20)$ of $400 \mu\text{atm}$; whereas the solid blue triangles and solid blue triangles with line are the fixed and linear temperature dependencies based on the results of Takahashi et al. (1993).

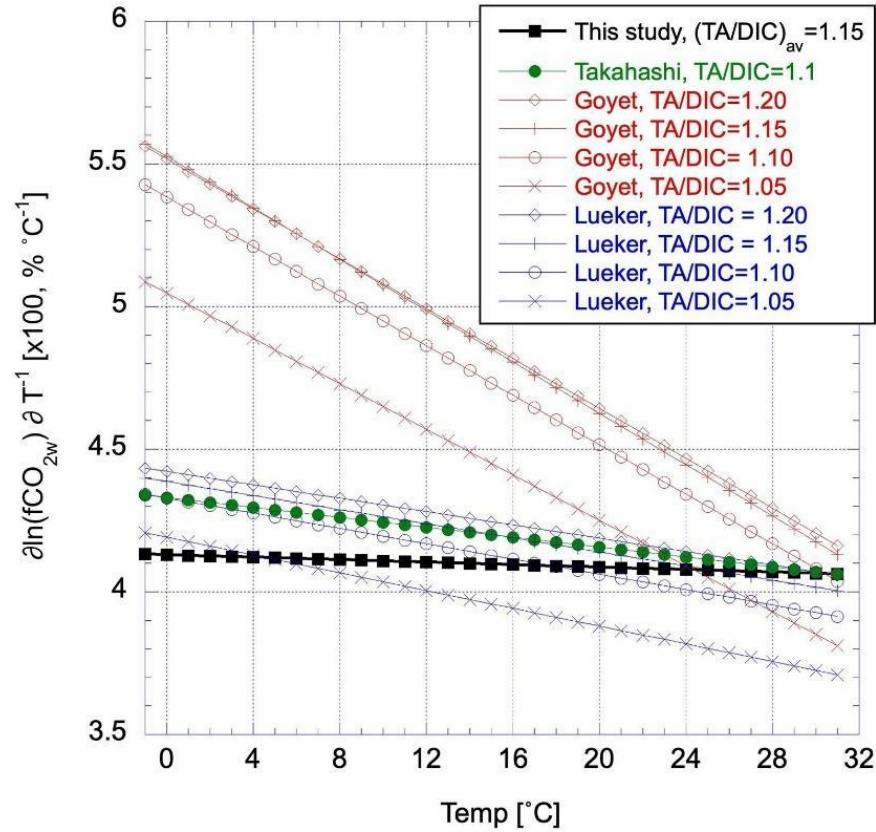


Figure 4. The temperature dependence of $\partial \ln(f\text{CO}_{2w}) / \partial T$ [$\times 100, \% \text{ } ^\circ\text{C}^{-1}$] plotted against temperature for different TA/DIC values (see legend). The upper red lines are the results of Goyet et al. (1993); the middle blue lines are the output of the CO2SYS program (Pierrot et al., 2006) using the carbonate dissociation constants of Lueker et al. (2000); the green line is the equation of Takahashi et al. (2009) with a TA/DIC = 1.1 and the black line shows the results of $\partial \ln(f\text{CO}_2(\text{TA}, \text{DIC})) / \partial T * 100$ from this study with an average TA/DIC = 1.15. The results of Goyet et al. (1993), and the CO2SYS output using the Lueker et al. (2000) constants, with SSS = 35, are for TA = 2310, and DIC = 2200, 2100, 2008, 1925 $\mu\text{mol kg}^{-1}$ yielding TA/DIC of 1.05, 1.1, 1.15, and 1.2, respectively.

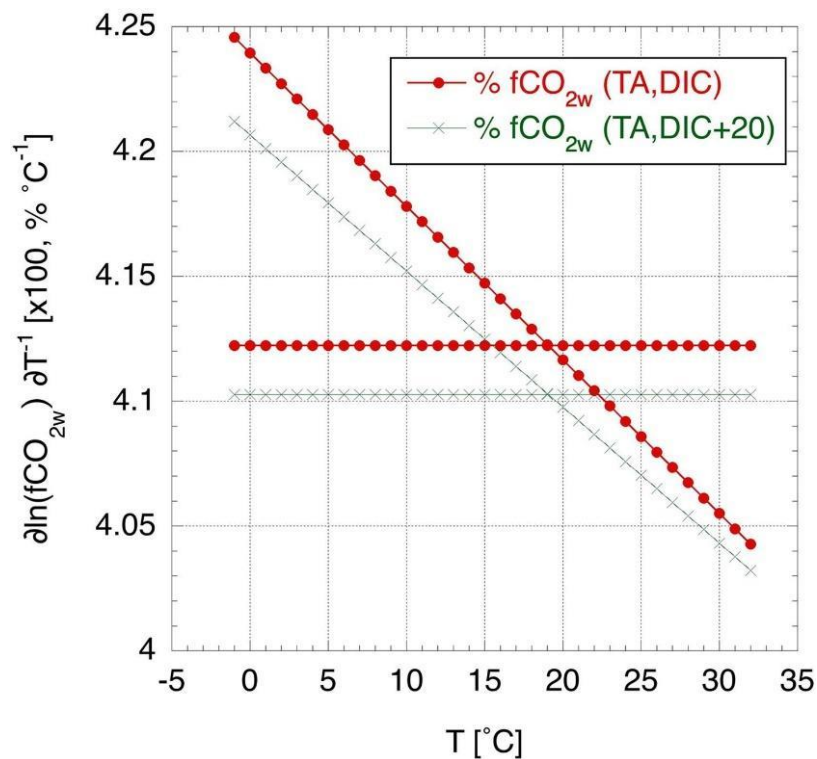


Figure 5. The effect of changing DIC on the temperature dependence. The red lines with circles are the observed constant and linear dependencies, $\partial \ln(f\text{CO}_{2w}) / \partial T$ [$\times 100, \% \text{ } ^\circ\text{C}^{-1}$], for the calculated $f\text{CO}_2(\text{TA}, \text{DIC})$ in this study whereas the solid lines with crosses are the constant and linear temperature dependencies after adding $20 \mu\text{mol kg}^{-1}$ DIC to the calculated values.

Table 1. Summary of regression statistics to determine the constant temperature dependence of fCO₂ in surface water based on linear regressions of ln(UW_fCO₂/disc_fCO₂(20)) versus (SST-20).

Cruise	EXPCODE	Year	Intercept (x100)	St_error Intercept (x100)	Slope (x100)	St_error Slope (x100)	R ²	e ^(intercept) (a)	#	# omitted
All data			-0.75	0.04	4.13	0.01	0.996	0.9925	2071	52
SAtl91_L1_L2	33 MW19910711	1991	-0.22	0.15	3.85	0.03	0.990	0.9978	124	7
EqPac-Spring92	33 MW19920226	1992	-4.76	1.35	4.51	0.16	0.878	0.9535	109	1
EqPac-Fall92	33 MW19920909	1992	-2.45	0.43	4.36	0.10	0.964	0.9758	67	2
NAtl93	33 MW19930705	1993	-0.01	0.19	4.17	0.03	0.994	0.9999	84	1
P18-94_CGC94	31DSCG94_3	1994	-0.76	0.59	3.82	0.09	0.956	0.9924	92	7
IO95_I8N	33 MW19950922	1995	-0.51	0.11	4.24	0.02	0.998	0.9949	109	0
A05-98_24N	33RO19980123	1998	-2.25	0.33	4.32	0.10	0.963	0.9777	72	1
GasEx-98_L2	33RO19980525	1998	-2.63	0.71	3.76	0.16	0.835	0.9741	111	0
NAtl-2003_A16N	33RO20030619	2003	-1.76	0.09	4.20	0.01	0.999	0.9826	85	2
SAtl-2005_A16S	33RO20050111	2005	-1.10	0.19	4.18	0.02	0.999	0.9890	38	1
GOMECC1-2007	33RO20070710	2007	1.42	0.22	4.06	0.03	0.995	1.0143	104	4
P18-2008	33RO20071215	2008	0.43	0.16	4.09	0.02	0.998	1.0043	73	1
A13.5-2010	33RO20100308	2010	-1.59	0.11	4.09	0.01	0.999	0.9842	51	0
GOMECC2(UW) ^b	33RO20120721	2012	-0.98	0.58	4.14	0.07	0.969	0.9903	118	1
GOMECC2(Sta) ^b	33RO20120721	2012	-0.77	0.37	4.11	0.05	0.983	0.9923	127	16
A16N2013	33RO20130803	2013	-0.44	0.18	4.05	0.03	0.992	0.9956	127	3
A16S2014	33RO20131223	2014	-2.00	0.12	4.13	0.01	0.999	0.9802	47	1
GOMECC3(Sta) ^b	33RO20170718	2017	2.26	1.21	3.83	0.12	0.908	1.0229	101	2
GOMECC3(UW) ^b	33RO20170718	2017	0.14	0.90	3.98	0.09	0.931	1.0014	134	2
A13.5-2020_transit (UW) ^b	33RO20200221	2020	1.42	0.31	3.89	0.05	0.988	1.0143	81	0
A13.5-2020_truncated	33RO20200321	2020	1.03	0.08	4.05	0.01	0.990	1.0103	217	0

(a) at 20°C: $UW_fCO_2 = e^{(Intercept)} disc_fCO_2$.

(b) UW: discrete samples from the scientific supply seawater line; Sta: discrete samples from the CTD/Niskin bottles at stations.

Table 2. Summary of difference between measured and calculated fCO₂ from TA and DIC^a, and its temperature dependence.

Cruise	EXPOCODE	Year	disc_fCO ₂ (2) (meas-cal)	St._dev	Count	UW_fCO ₂ (SST) (meas-cal)	St_dev	Icept x100	Count	Temp. dependence Slope x100
All data			-1.35	6.81	1788	-2.86	9.23	0.020	1617	4.10
SAtl91_L1_L2	33 MW19910711	1991	-4.87	8.11	23	-7.48	11.1	0.16	22	4.11
EqPac-Spring92	33 MW19920226	1992	1.5	6.46	115	-2.14	12.62	-2.1	97	4.29
EqPac-Fall92	33 MW19920909	1992	2.94	5.92	87	-4.4	9.55	-0.48	56	4.16
NAtl93	33 MW19930705	1993	2.79	3.87	64	4.23	6.22	-1	77	4.13
P18-94_CGC94	31DSCG94_3	1994	-1.33	6.79	132	-8.38	9.02	4.6	76	4.16
IO95_I8N	33 MW19950922	1995	-1.53	4.73	97	-1.26	4.28	0.1	90	4.11
A05-98_24N	33RO19980123	1998	3.5	5.69	78	-1.73	5.6	0.05	81	4.07
NAtl-2003_A16N	33RO20030619	2003	-0.55	5.04	83	-3.95	6.23	0.04	83	4.13
SAtl-2005_A16S	33RO20050111	2005	-0.30	7.31	37	-2.38	7.27	-0.21	39	4.17
GOMECC1-2007	33RO20070710	2007	-1.85	3.69	99	4.83	8.91	0.02	103	4.06
P18-2008	33RO20071215	2008	2.85	6.53	64	-1.96	7.98	-0.51	64	4.17
A13.5-2010	33RO20100308	2010	-1.08	4.19	119	-4.07	6.18	-0.75	34	4.15
GOMECC2(UW) ^b	33RO20120721	2012	1.8	9.19	55	0.9	13.2	0.45	54	4.01
GOMECC2(Sta) ^b	33RO20120721	2012	2.85	7.01	128	2.97	11.2	0.5	116	4.03
A16N2013	33RO20130803	2013	-3.47	5.26	115	-2.97	7.12	0.09	107	4.11
A16S2014	33RO20131223	2014	1.04	7.07	43	-0.98	10.58	-0.04	34	4.14
GOMECC3(disc_sta) ^b	33RO20170718	2017	-1.60	5.42	101	-2.47	6.81	0.24	99	4.06
GOMECC3(disc_UW) ^b	33RO20170718	2017	-4.66	6.10	138	-8.32	8.81	0.54	138	4.02
A13.5-2020_trunc	33RO20200321	2020	-9.04	3.88	220	-7.88	4.70	0.54	135	4.03

(a) Calculations done using CO2SYSV2.1 for Excel (Pierrot et al., 2006) with carbonate dissociation constants as provided in Lueker et al. (2000); the borate-salinity ratio of Uppström (1974); the acidity constant of HSO₄ from Dickson (1990); and association constant of HF from Perez and Fraga (1987).

(b) UW: discrete samples from the scientific seawater line; Sta: discrete samples from the CTD/Niskin bottles at stations.