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**Carbonate chemistry
inconsistencies**

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On CO₂ perturbation experiments: over-determination of carbonate chemistry reveals inconsistencies

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Abstract

Seawater carbonate chemistry is typically calculated from two measured parameters. Depending on the choice of these input parameters, discrepancies in calculated $p\text{CO}_2$ have been recognized by marine chemists, but the significance of this phenomenon for CO_2 perturbation experiments has so far not been determined. To mimic different $p\text{CO}_2$ scenarios, two common perturbation methods for seawater carbonate chemistry (changing either DIC or TA) were applied using state-of-the-art protocols and equipment. The carbonate system was over-constrained by measuring DIC, TA, pH, and $p\text{CO}_2$. Calculated $p\text{CO}_2$ matched measured $p\text{CO}_2$ if pH and TA or pH and DIC were chosen as input parameters, whereas $p\text{CO}_2$ calculated from TA and DIC was considerably lower than measured values. This has important implications for CO_2 perturbation experiments. First, calculated $p\text{CO}_2$ values may not be comparable if different input parameters were used. Second, responses of organisms to acidification may be overestimated when using TA and DIC for calculations. This is especially troublesome for experiments with calcifiers, as carbonate ion concentration and thus calcite or aragonite saturation state are overestimated. We suggest refraining from measuring TA and DIC only and rather include pH as input parameter for carbonate chemistry calculations.

1 Introduction

Since the beginning of the industrial revolution, CO_2 emissions from the burning of fossil fuels and changes in land use have increased atmospheric CO_2 levels from preindustrial values of $280 \mu\text{atm}$ to currently $385 \mu\text{atm}$. Values are expected to rise to $750 \mu\text{atm}$ (IPCC scenario IS92a, ARP4, 2007) or even beyond $1000 \mu\text{atm}$ by the end of this century (Raupach et al., 2007). In addition to its contribution to the broadly discussed greenhouse effect, a significant proportion of anthropogenic CO_2 has been taken up by the world's oceans, causing a shift of the carbonate chemistry towards

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higher CO₂ concentration and lower pH (Broecker et al., 1971). This process, commonly referred to as “ocean acidification”, is already occurring and expected to intensify in the future (Caldeira and Wickett, 2003; Wolf-Gladrow et al., 1999). Ocean acidification will affect marine biota in many different ways (see Fabry et al., 2008, Rost et al., 2008 for reviews).

To shed light on potential responses of organisms and ecosystems, numerous national and international research projects (e.g. EPOCA, OCB, Doney et al., 2009 for details) have recently been initiated, which incorporate a wide spectrum of scientific disciplines such as chemical oceanography, paleoceanography, marine ecology and physiology. An essential part of ocean acidification research is based on CO₂ perturbation experiments, which represent the prime tool for studying responses of key species and marine communities. It is commonly accepted practise to only measure two of the carbonate chemistry parameters (TA, DIC, pH, pCO₂) and calculate the others (including CO₂, HCO₃⁻ and CO₃²⁻; Dickson et al., 2007, Millero et al., 1993). While TA and DIC have been favoured, as sample preservation and measurement are relatively easy, pH has been under debate because of intricacies concerning scales and measurement protocols (Dickson, 2010). For calculations, knowledge of the first and second dissociation constants of carbonic acid (pK₁ and pK₂) is needed, which have been determined several times for a wide range of temperature and salinity conditions (Dickson, 2010).

Several over-constrained studies (i.e. measurement of more than two carbonate system parameters) revealed discrepancies between measured and calculated carbonate chemistry parameters, which differed depending on the pair of input parameters used for calculations (Dickson and Millero, 1987, McElligott et al., 1998, Millero et al., 2002). These datasets were produced by marine chemists, typically using elaborate protocols and thus measuring with very high precision and accuracy. Although generally desirable, such sophistication is currently not achieved in laboratory routine by experimentators in the ocean acidification community. As the experimental setup and data quality of these studies differ from those of the ocean acidification community, implications

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of the inconsistencies described above are currently unknown. Therefore we manipulated the carbonate chemistry of natural seawater and over-constrained the system by measuring TA, DIC, pH and $p\text{CO}_2$ using state-of-the-art protocols and equipment of the ocean acidification community (Gattuso et al., 2010).

2 Material and methods

2.1 Media preparation

Sterile-filtered ($0.2\ \mu\text{m}$) North Sea seawater containing $7.2\ \mu\text{mol L}^{-1}$ silicate was enriched with vitamins and trace metals according to f/2 media (Guillard and Ryther, 1962) as well as with nitrate and phosphate. Final values of nitrate and phosphate were $111.5\ \mu\text{mol L}^{-1}$ and $5.85\ \mu\text{mol L}^{-1}$ respectively. Nutrients were measured colourimetrically using a continuous flow analyzer (Evolution III, Alliance Instruments, Salzburg, Austria). The salinity was 32.38 ± 0.003 (measured with a Guildline Autosol 8400B, Ontario, Canada).

2.2 DIC manipulations

Manipulations were conducted at $15 \pm 0.2\ ^\circ\text{C}$ in 2 L borosilicate bottles equipped with glass frits for aeration. The media were sparged continuously with humidified, $0.2\ \mu\text{m}$ -filtered air of different partial pressures of CO_2 (180 and $1000\ \mu\text{atm}$). Gas flow rates were $130 \pm 10\ \text{mL min}^{-1}$. Gas mixtures were generated using a custom-made gas flow controller. CO_2 -free air ($< 1\ \text{ppm CO}_2$; Dominick Hunter, Willich, Germany) was mixed with pure CO_2 (Air Liquide Deutschland, Düsseldorf, Germany) by a mass flow controller based system (CGM 2000 MCZ Umwelttechnik, Bad Nauheim, Germany). The CO_2 concentration was regularly controlled with a non-dispersive infrared analyzer system (LI6252, LI-COR Biosciences, Bad Homburg, Germany) calibrated with CO_2 -free air and purchased gas mixtures of 150 ± 10 and $1000 \pm 20\ \text{ppmv CO}_2$ (Air

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Liquide Deutschland, Düsseldorf, Germany). Seawater samples were taken after 48 h to ensure equilibration.

2.3 Alkalinity manipulation

Carbonate chemistry was adjusted by addition of calculated amounts of HCl or NaOH (1 N Titrisol, Merck, Darmstadt, Germany) to seawater for which DIC was known. The manipulated media were stored in 2 L borosilicate bottles which were sealed immediately with Teflon-lined screw caps without head space to avoid CO₂ exchange with the atmosphere.

2.4 Sampling and measurements

Samples for total alkalinity (TA) were 0.6 µm-filtered, stored in 150 mL borosilicate bottles at 3 °C and analysed within a week. TA was calculated from linear Gran plots (Gran, 1952) after duplicate potentiometric titration (Brewer et al., 1986) using a TitroLine alpha plus (Schott Instruments, Mainz, Germany). Average precision was ± 5 µmol kg⁻¹. Certified Reference Materials (CRMs, Batch No. 54) supplied by A. Dickson (Scripps Institution of Oceanography, USA) were used to correct for inaccuracies of the measurements.

Dissolved inorganic carbon (DIC) samples were filtered through 0.2 µm cellulose-acetate filters and stored in 5 mL gas-tight borosilicate bottles at 3 °C. Within one week, DIC was measured colourimetrically in triplicates with a TRAACS CS800 autoanalyzer (Seal, Mequon, USA) with a precision of ± 5 µmol kg⁻¹. Shifts in DIC due to CO₂ exchange were prevented by opening the storage vials less than one minute prior to each measurement. CRMs (Batch No. 54) supplied by A. Dickson were used to correct for inaccuracies of the measurements.

Seawater pH values were determined by two different approaches, potentiometrically (on the NBS scale) and spectrophotometrically (on the total scale). For the potentiometric measurement, the glass reference electrode (IOline, Schott Instruments) was

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two-point calibrated prior to every set of measurements. Average precision was found to be ± 0.02 pH units. Seawater pH on the total scale was measured spectrophotometrically (Clayton and Byrne, 1993, Dickson et al., 2007) using a temperature-controlled Cary 4000 UV-VIS-NIR spectrophotometer (Varian, Palo Alto, USA). Absorption measurements were corrected for pH changes due to dye addition and background absorption. Average precision was found to be ± 0.003 pH units. Data accuracy of both pH measurements was corrected using Tris-based pH references materials (batch 2) provided by A. Dickson. Carbonate chemistry calculations were based on spectrophotometric pH measurements on the total scale.

Aqueous $p\text{CO}_2$ was determined using a Membrane-Inlet Mass Spectrometer (MIMS, Tortell, 2005), which consists of a thermostated cuvette being connected to a sector field multi-collector MS (Isoprime; GV Instruments, England). The MIMS was calibrated for CO_2 by injections of known amounts of NaHCO_3 into 8 ml of 0.2 N HCl (Schulz et al., 2006). The CO_2 baseline was determined by addition of 20 μL 10 N NaOH. CO_2 concentrations were measured with an average precision of $\pm 0.13 \mu\text{mol kg}^{-1}$ ($n = 15$).

2.5 Calculations of carbonate chemistry

Calculations were performed with the program CO_2 sys (Lewis and Wallace, 1997) and verified with the MATLAB files based on Zeebe and Wolf-Gladrow (2001). Five pairs of dissociation constants were compared (Goyet and Poisson, 1989; Hanson et al., 1973 refit by Dickson and Millero, Mehrbach et al., 1973 refit by Dickson and Millero, 1989, 1989; Millero et al., 2006; Roy et al., 1990). Unless stated otherwise, the dissociation constants of carbonic acid of Roy et al. (1990) were used for calculations. Dissociation constants for H_2SO_4 were taken from Dickson (1990). CO_2 concentrations obtained with MIMS were converted to $f\text{CO}_2$ by applying Henry's law (Weiss, 1974) and further converted to $p\text{CO}_2$ using CO_2 sys (Lewis and Wallace, 1997).

2.6 Error propagation in determination of the carbonate system

Several components of the carbonate system (DIC, TA, pH, $p\text{CO}_2$) can be measured quite accurately whereas others (HCO_3^- , CO_3^{2-}) have to be calculated. The accuracy of the measurements depends on sample preparation, instrumentation and methodology. In order to judge whether over-constrained measurements are consistent, knowledge of measurement errors propagation is required. Dickson and Riley (1978) investigated the propagation of variances in the carbonate system using the equations of Park (1969) as republished in amended form by Skirrow (1975), using carbonate alkalinity instead of total alkalinity. For small variances, the variance in the calculated variable Y , $\text{var}(Y)$, is given as the sum over the squares of the partial derivatives of Y with respect to the measured quantities X_i times the variances of X_i :

$$\text{var}(Y) = \sum_i (\partial Y / \partial X_i)^2 \text{var}(X_i). \quad (1)$$

The partial derivatives can be calculated using the programs mentioned above. For DIC manipulations, i.e. keeping TA constant while increasing DIC, one obtains partial derivatives of $p\text{CO}_2$ with respect to DIC or TA that vary strongly with DIC or $p\text{CO}_2$. At $T = 15^\circ\text{C}$, $S = 32.38$ and $p\text{CO}_2$ in the range between 180 and 1000 μatm , they can be approximated by the following linear functions:

$$(\partial p\text{CO}_2 / \partial \text{DIC})_{\text{TA}} \approx 0.00732 p\text{CO}_2 - 0.4 \quad (2)$$

$$(\partial p\text{CO}_2 / \partial \text{TA})_{\text{DIC}} \approx -0.00674 p\text{CO}_2 + 0.5 \quad (3)$$

where $p\text{CO}_2$ is in μatm and the partial derivatives in $\mu\text{atm} (\mu\text{mol kg}^{-1})^{-1}$. Similar calculations can be performed for the input pairs DIC and pH or TA and pH. The corresponding partial derivatives also vary strongly with $p\text{CO}_2$ and can be approximated for the conditions mentioned above by the following linear functions:

$$(\partial p\text{CO}_2 / \partial \text{DIC})_{\text{pH}} \approx 0.00042 p\text{CO}_2 \quad (4)$$

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$$(\partial p\text{CO}_2/\partial \text{pH})_{\text{DIC}} \approx -2.3 p\text{CO}_2 - 54 \quad (5)$$

$$(\partial p\text{CO}_2/\partial \text{TA})_{\text{pH}} \approx 0.00042 p\text{CO}_2 \quad (6)$$

$$(\partial p\text{CO}_2/\partial \text{pH})_{\text{TA}} \approx -2.44 p\text{CO}_2 - 91.4 \quad (7)$$

where $p\text{CO}_2$ is in μatm and the partial derivatives in $\mu\text{atm} (\mu\text{mol kg}^{-1})^{-1}$ or in $\mu\text{atm per pH unit}$, respectively.

For standard deviations of $5 \mu\text{mol kg}^{-1}$ in DIC and TA and 0.003 in pH, one obtains the following standard deviations in $p\text{CO}_2$: For measured DIC and TA, standard deviations are $7 \mu\text{atm}$ at low and $47 \mu\text{atm}$ at high $p\text{CO}_2$. For measured DIC and pH, standard deviations are $2 \mu\text{atm}$ at low and $7 \mu\text{atm}$ at high $p\text{CO}_2$ and for measured TA and pH, $2 \mu\text{atm}$ at low and $8 \mu\text{atm}$ at high $p\text{CO}_2$. Variances in temperature ($\pm 0.2^\circ\text{C}$), salinity (± 0.003), and equilibrium constants (± 0.004 for pK_1 and ± 0.006 for pK_2 , Roy et al., 1993) could increase the standard deviation of $p\text{CO}_2$ by less than $10 \mu\text{atm}$ for any of these parameters. In addition to the propagation of variances one may consider the propagation of systematic errors. For small errors one can use

$$\Delta p\text{CO}_2 = (\partial p\text{CO}_2/\partial \text{DIC})_{\text{TA}} \Delta \text{DIC} + (\partial p\text{CO}_2/\partial \text{TA})_{\text{DIC}} \Delta \text{TA} \quad (8)$$

for estimating the error in $p\text{CO}_2$ for the measured pair (DIC, TA); analogous expressions apply for the other pairs. The correlations of the errors of the measured parameters were chosen to give maximum errors in the derived parameter: At $p\text{CO}_2 = 200 \mu\text{atm}$ and errors $\Delta \text{DIC} = -5 \mu\text{mol kg}^{-1}$ and $\Delta \text{TA} = +5 \mu\text{mol kg}^{-1}$, one obtains $\Delta p\text{CO}_2 = -10 \mu\text{atm}$. At $p\text{CO}_2 = 1000 \mu\text{atm}$ and the same errors in DIC and TA, the error $\Delta p\text{CO}_2 = -66 \mu\text{atm}$ is much higher. For the input pair DIC and pH, errors $\Delta \text{DIC} = -5 \mu\text{mol kg}^{-1}$ and $\Delta \text{pH} = +0.003$ lead to $\Delta p\text{CO}_2 = -2 \mu\text{atm}$ and $\Delta p\text{CO}_2 = -9 \mu\text{atm}$ at low and high $p\text{CO}_2$, respectively. For the input pair TA and pH, the errors $\Delta \text{TA} = -5 \mu\text{mol kg}^{-1}$ and $\Delta \text{pH} = +0.003$ lead to $\Delta p\text{CO}_2 = -2 \mu\text{atm}$ and $\Delta p\text{CO}_2 = -10 \mu\text{atm}$ at low and high $p\text{CO}_2$, respectively. The magnitude of errors in $p\text{CO}_2$ is smaller when errors of DIC, TA, and pH are correlated differently.

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3 Results

In the DIC manipulations, the aeration of the seawater led to equilibration after 10 h (Fig. 1), yielding final DIC concentrations of $1946 \mu\text{mol kg}^{-1}$ at low and $2255 \mu\text{mol kg}^{-1}$ at high $p\text{CO}_2$, while TA stayed quasi-constant at $2388 \mu\text{mol kg}^{-1}$ (Table 1). Corresponding pH_{total} values were 8.29 and 7.72 at low and high $p\text{CO}_2$, respectively. TA manipulation by addition of base or acid resulted in TA values of $2641 \mu\text{mol kg}^{-1}$ and $2277 \mu\text{mol kg}^{-1}$ at low and high $p\text{CO}_2$, respectively (Table 1). Corresponding pH_{total} values were 8.32 at low and 7.61 at high $p\text{CO}_2$, while DIC concentrations were $2216 \mu\text{mol kg}^{-1}$ and $2186 \mu\text{mol kg}^{-1}$, respectively.

The calculations based on the different carbonate chemistry parameters measured revealed discrepancies in $p\text{CO}_2$ between different input pairs, which increased systematically with increasing $p\text{CO}_2$. As shown in Table 1, the $p\text{CO}_2$ calculated from DIC and TA was considerably lower than the $p\text{CO}_2$ calculated from DIC and pH_{total} or from TA and pH_{total} , the latter pairs yielding comparable results. Furthermore, calculated $p\text{CO}_2$ based on pairs involving pH_{total} compare well with those values directly measured in air (180 ± 10 and $1000 \pm 20 \mu\text{atm CO}_2$) and by means of MIMS (Fig. 2). In contrast, $p\text{CO}_2$ values calculated from TA and DIC were up to $377 \mu\text{atm}$ lower than measured. The same phenomenon was observed in both, DIC and TA manipulations (Table 1).

Calculations using five different pairs of dissociation constants (Mehrbach et al., 1973, Hansson et al., 1973, refit of both by Dickson and Millero, 1989, Goyet and Poisson, 1989, Roy et al., 1990, Millero et al., 2006) led to slightly different values for calculated $p\text{CO}_2$ values (difference $\leq 14 \mu\text{atm}$ at low and $\leq 48 \mu\text{atm}$ at high $p\text{CO}_2$). While the discrepancies in calculated $p\text{CO}_2$ for different input pairs were smallest using the constants by Roy et al. (1990), the best match to the measured $p\text{CO}_2$ by means of MIMS was obtained with the constants determined by Hansson et al. (1973) refit by Dickson and Millero (1989). Despite these differences, the observed trend of increasing discrepancies with increasing $p\text{CO}_2$ (Table 1, Fig. 2) was found for all constant pairs.

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Two different methods for measurement of pH were applied, which differ in precision (± 0.003 for the spectrophotometric and ± 0.02 pH units for the potentiometric measurements). To compare the effect of these approaches on $p\text{CO}_2$ estimates, either pH_{total} or pH_{NBS} was combined with TA. Calculations yielded differences of $3 \mu\text{tam}$ at low and $117 \mu\text{tam}$ at high $p\text{CO}_2$. Also, the effect of imprecision (± 0.02) was highest under high $p\text{CO}_2$ ($\pm 62 \mu\text{tam}$). These differences are, however, minor when compared to the discrepancies described above.

4 Discussion

The over-determination of the carbonate system revealed discrepancies between measured and calculated $p\text{CO}_2$, which occurred in DIC as well as TA manipulations. Depending on the choice of input parameters, calculated $p\text{CO}_2$ deviated by up to $377 \mu\text{tam}$ from measured values. Using the input pair TA and DIC, these discrepancies increased proportionally with $p\text{CO}_2$ while calculations involving pH compare well with the measured $p\text{CO}_2$. Surprisingly, although TA and DIC provide good $p\text{CO}_2$ estimates when combined with pH, the same both parameters yield erroneous results when directly combined as input parameters.

In the following, a number of possible causes for this phenomenon is discussed. As two different calculation programs obtained the same results, the inconsistency in $p\text{CO}_2$ values cannot be explained by program-specific differences. The choice of dissociation constants has been debated comprehensively (Dickson, 2007, Millero et al., 2002, Lee et al., 2000). However, differences in calculated $p\text{CO}_2$ values originating from the use of different constants are about an order of magnitude smaller than the described phenomenon. As will be argued, errors in a single input parameter (e.g. TA) cannot explain the discrepancies found. Moreover, the changes in TA due to typical additives of culture media (Probert and Houdan, 2004) cannot cause the discrepancies described, as the phenomenon was also observed in an experiment where natural seawater from the Gulf of Eilat without additives was used (Schneider and Erez, 2006; Fig. 3).

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Errors in the determination of TA, DIC, and pH are another potential cause of the discrepancies. Since the phenomenon is independent of the method of manipulation, neither TA nor DIC measurement errors alone can cause the offset. Furthermore, both TA and DIC lead to relatively good results when combined with pH as input parameters. Thus, a directional error, co-occurring in all three measurements of TA, DIC and pH, would have to be assumed, if measurement accuracy and/or precision were responsible for the discrepancies between the $p\text{CO}_2$ values derived from different input pairs (Fig. 2). Besides the unlikelihood of this, precision of the measurements in this study was too high to serve as an explanation (compare Sect. 2.6), as it could only reduce the mean discrepancies from 40 to 30 μatm at low and from 309 to 243 μatm at high $p\text{CO}_2$.

Regarding pH measurements, the precision of the spectrophotometric method (Clayton and Byrne, 1993) was considerably better than the one of the potentiometric approach (see also Clayton et al., 1995), a finding also emphasized by Dickson (2010). Another advantage of the spectrophotometric method is the direct calibration on the total scale (using Tris-based pH reference materials provided by A. Dickson) as opposed to the NBS scale (potentiometric method). We therefore suggest using the spectrophotometric method, if feasible. In this context, however, it is important to note that even when pH_{NBS} was used, the calculated $p\text{CO}_2$ values are much closer to the measured values than those derived from TA and DIC.

The discrepancies we found (Table 1, Fig. 2) were comparable in magnitude to another over-constrained perturbation experiment (Schneider and Erez, 2006). To illustrate this, $p\text{CO}_2$ outputs from their data (phosphate and silicate concentrations for the Gulf of Eilat were taken from Mackey et al., 2009) were combined with our data (Fig. 3) and yielded virtually the same relationship. A number of other over-constrained studies have also reported discrepancies, but in these datasets the phenomenon was found to be significantly smaller (Dickson and Millero, 1987; Lee et al., 2000; McElligott et al., 1998; Millero et al., 2002, 2006). It is noteworthy that the smaller discrepancies were published by researchers of the marine chemistry community whereas the larger

discrepancies were found in datasets produced within the ocean acidification community (Schneider and Erez, 2006, this study). It is therefore likely, that differences in measuring protocols play a considerable role with regard to the magnitude of the discrepancies (see also McElligott et al., 1998). As shown in Sect. 2.6., calculated $p\text{CO}_2$ is particularly sensitive to measurement errors if TA and DIC are used as input parameters. This finding supports the notion that measurement errors can enlarge the discrepancies. Since the phenomenon is immanent in all studies mentioned above, however, measuring protocols and choice of equipment cannot be its cause.

It has been suggested that errors in pK_1 and pK_2 may cause the inconsistencies (Dickson and Millero, 1987). Since the discrepancies are larger at higher $p\text{CO}_2$, this also implies that pK_1 and/or pK_2 vary as a function of $[\text{CO}_2]$ (Lee et al., 2000). Although “this contradicts the current understanding of the carbonate system” (Lee et al., 2000), Millero et al. (2002) suggested a dependency of the constants on DIC. As the phenomenon was also observed at constant DIC and variable TA (Table 1, Fig. 2), our data does not support this idea. However, the putative dependency could be on the speciation-dependent parameters $[\text{CO}_2]$, $[\text{CO}_3^{2-}]$ or pH, while a dependency on $[\text{HCO}_3^-]$ is unlikely due to relatively small concentration changes in this DIC-species.

Regardless of the reason for this phenomenon, the latter has, at any rate, consequences for ocean acidification research. First, published $p\text{CO}_2$ values may not be comparable, if different input parameters were measured. Second, as calculated $p\text{CO}_2$ values based on TA and DIC are underestimated, an organism’s respective sensitivity to acidification is overestimated when this input pair is used for calculations. This is especially important at $p\text{CO}_2$ levels $\geq 750 \mu\text{atm}$, which are typically used for the year 2100 scenario and therefore crucial for all CO_2 perturbation experiments. Third, if TA and DIC are used for calculations, the $[\text{CO}_3^{2-}]$ and therewith calcite and aragonite saturation states (Ω) are overestimated. Since a considerable part of ocean acidification research is concerned with marine calcifiers (Fabry et al., 2008), the saturation state must receive special attention. The error in Ω becomes increasingly important when approaching undersaturation, as calcareous shells of e.g. coccolithophores or

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foraminifera can dissolve. This renders an accurate measurement of calcite quotas and calcification rates impossible. We conclude that it is advisable use pH and TA or pH and DIC for calculating the carbonate chemistry and, if possible, to measure and report additional parameters.

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Table 1. Measured carbonate chemistry parameters (pH, DIC, TA and CO₂) and resulting pCO₂ values calculated from different input parameters using the constants of Roy et al., 1990. Standard deviation for pH_{NBS} denote average precision (n = 30), other errors denote standard deviation of technical replicates.

| | | Measured parameter | | | | | Calculated pCO ₂ (µatm) | | | |
|------------------|--------------------------|--------------------|---------------------|---------------------------------|--------------------------------|---|------------------------------------|-------------------------------|------------------------------|-------------------------------|
| | | pH _{NBS} | pH _{total} | DIC (µmol kg ⁻¹) | TA (µmol kg ⁻¹) | CO ₂ (µmol kg ⁻¹) | pCO ₂ (MIMS) | pCO ₂ (TA; DIC) | pCO ₂ (TA; pH) | pCO ₂ (DIC; pH) |
| DIC manipulation | low pCO ₂ | 8.38 ± 0.02 | 8.252 ± 0.005 | 1945 ± 7 | 2388 ± 2 | 8.34 ± 0.14 | 205 | 152 | 243 | 231 |
| | | 8.39 ± 0.02 | 8.319 ± 0.001 | 1946 ± 7 | 2385 ± 3 | 7.82 ± 0.23 | 203 | 154 | 200 | 194 |
| | | 8.39 ± 0.02 | 8.305 ± 0.002 | 1946 ± 4 | 2383 ± 3 | 7.73 ± 0.23 | 219 | 155 | 208 | 201 |
| | high pCO ₂ | 7.91 ± 0.02 | 7.735 ± 0.001 | 2254 ± 1 | 2396 ± 1 | 39.31 ± 0.44 | 1042 | 693 | 965 | 945 |
| | | 7.88 ± 0.02 | – | 2254 ± 1 | 2386 ± 1 | 38.10 ± 0.02 | 1000 | 742 | – | – |
| | | 7.89 ± 0.02 | 7.712 ± 0.000 | 2256 ± 6 | 2388 ± 3 | 42.59 ± 0.02 | 1117 | 740 | 1021 | 1000 |
| TA manipulation | low pCO ₂ | 8.46 ± 0.02 | 8.313 ± 0.003 | 2211 ± 6 | 2643 ± 1 | 9.06 ± 0.07 | 259 | 203 | 227 | 224 |
| | | 8.48 ± 0.02 | 8.318 ± 0.012 | 2217 ± 6 | 2642 ± 0 | 9.10 ± 0.04 | 268 | 208 | 223 | 221 |
| | | 8.48 ± 0.02 | 8.317 ± 0.000 | 2220 ± 4 | 2640 ± 3 | 8.60 ± 0.08 | 238 | 212 | 224 | 222 |
| | high pCO ₂ | 7.72 ± 0.02 | 7.616 ± 0.004 | 2186 ± 2 | 2276 ± 1 | 47.48 ± 1.63 | 1202 | 925 | 1231 | 1210 |
| | | 7.81 ± 0.02 | 7.610 ± 0.004 | 2180 ± 4 | 2278 ± 3 | 47.51 ± 0.23 | 1247 | 874 | 1251 | 1224 |
| | | 7.79 ± 0.02 | 7.617 ± 0.013 | 2186 ± 1 | 2276 ± 1 | 47.89 ± 0.02 | 1257 | 920 | 1230 | 1208 |

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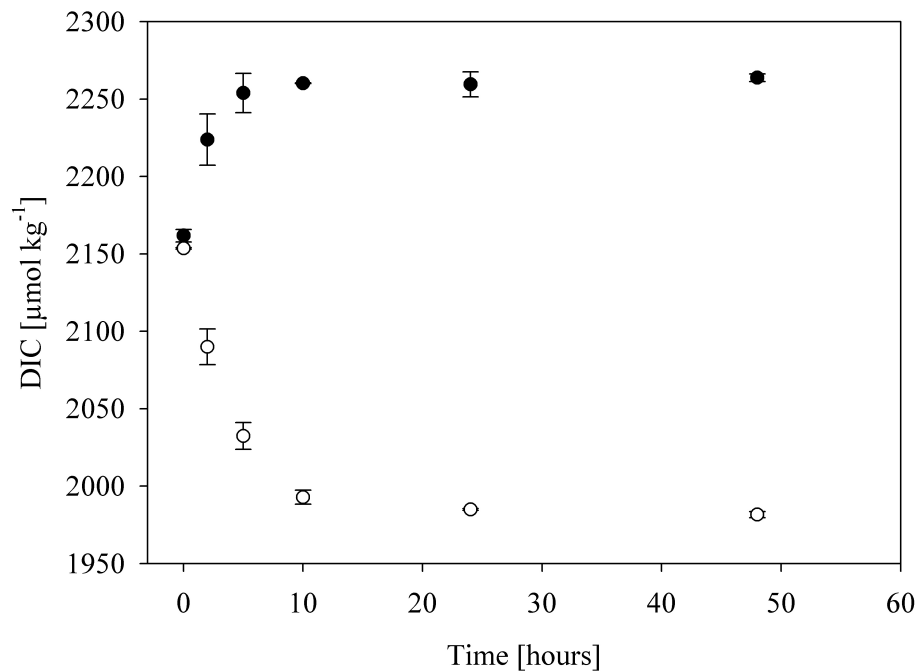


Fig. 1. Equilibration kinetics in DIC manipulation experiments represented by changes in DIC at low (open circles) and high $p\text{CO}_2$ (filled circles).

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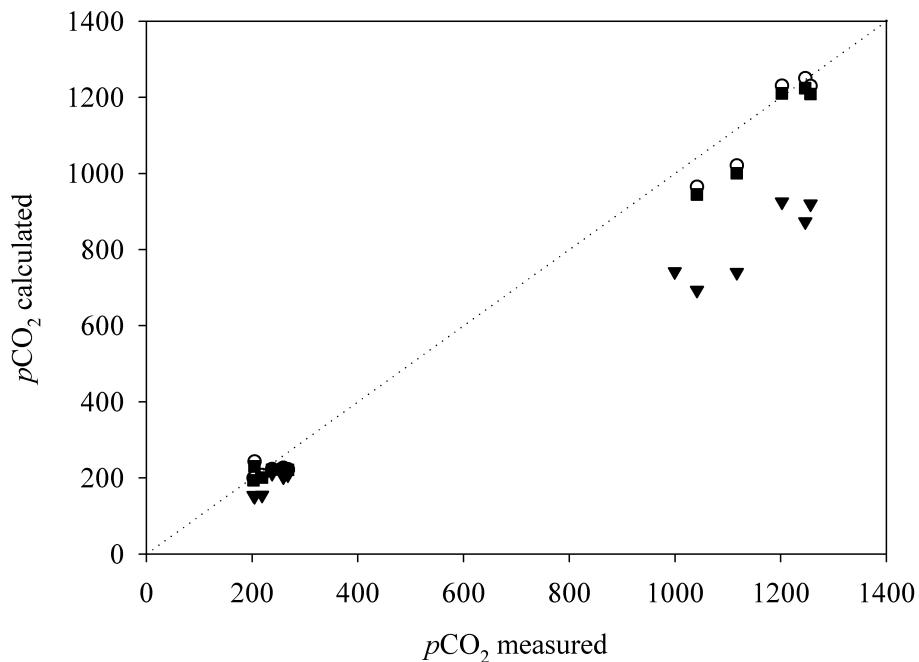


Fig. 2. Calculated $p\text{CO}_2$ from different input parameters (triangles: TA and DIC, circles: TA and pH, squares: DIC and pH) versus measured $p\text{CO}_2$ values.

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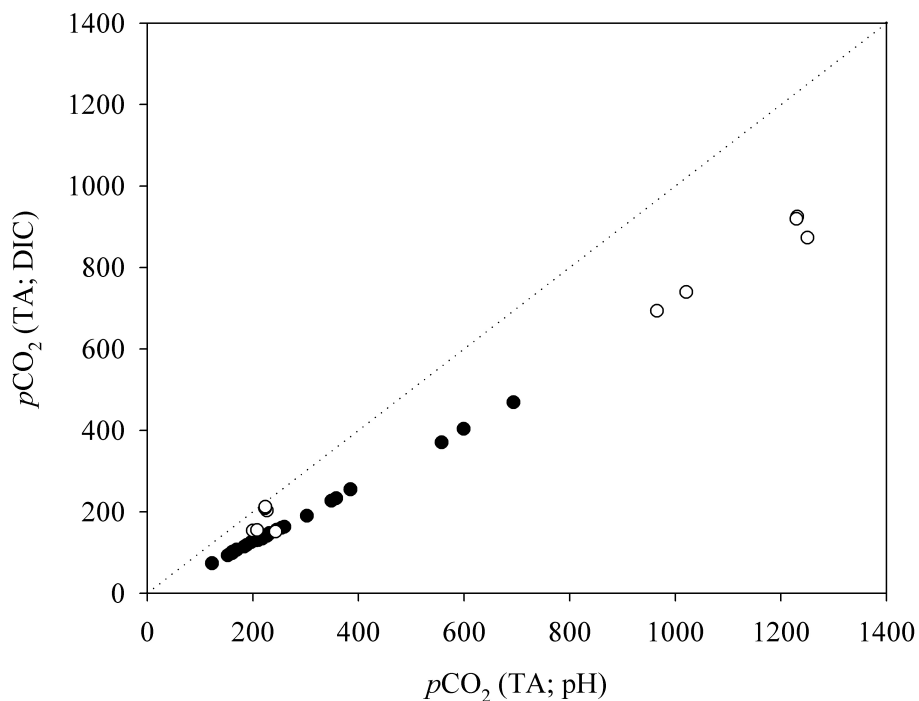


Fig. 3. Calculated $p\text{CO}_2$ (TA; DIC) versus calculated $p\text{CO}_2$ (TA; pH) from this study (open circles) and from Schneider and Erez 2006 (closed circles). The discrepancies (deviations from 1:1 line) increase with $p\text{CO}_2$.

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