**Biogeosciences
Discussions**

Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies

C. J. M. Hoppe, G. Langer, S. D. Rokitta, D. A. Wolf-Gladrow, and B. Rost

Alfred Wegener Institute for Polar and Marine Research, 27570 Bremerhaven, Germany

Correspondence to: C. J. M. Hoppe (clara.hoppe@awi.de)

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Abstract

The growing field of ocean acidification research is concerned with the investigation of organisms' responses to increasing pCO_2 values. One important approach in this context is culture work using seawater with adjusted CO_2 levels. As aqueous pCO_2 is difficult to measure directly in small scale experiments, it is generally calculated from two other measured parameters of the carbonate system (often A_T, C_T or pH). Unfortunately, the overall uncertainties of measured and subsequently calculated values are often unknown. Especially under high pCO_2, this can become a severe problem with respect to the interpretation of physiological and ecological data. In the few datasets from ocean acidification research where all three of these parameters were measured, pCO_2 values calculated from A_T and C_T are typically about 30 % lower (i.e. ∼ 300 µatm at a target pCO_2 of 1000 µatm) than those calculated from A_T and pH or C_T and pH. This study presents and discusses these discrepancies as well as likely consequences for the ocean acidification community. Until this problem is solved, one has to consider that calculated parameters of the carbonate system (e.g. pCO_2, calcite saturation state) may not be comparable between studies, and that this may have important implications for the interpretation of CO_2 perturbation experiments.

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 ppm to currently 390 ppm (http://www.esrl.noaa.gov/gmd/ccgg/trends; data by Tans & Keeling, NOAA/ESRL). Values are expected to rise to 750 ppm (IPCC scenario IS92a, IPCC, 2007) or even beyond 1000 ppm 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 ocean, causing a shift of the carbonate chemistry towards higher CO_2

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

⁵ To shed light on potential responses of organisms and ecosystems, numerous national and international research projects have recently been initiated (Doney et al., 2009 for details). An essential part of OA research is based on CO_2 perturbation experiments, which represent the primary tool for studying responses of key species and marine communities to acidification of seawater. Marine biologists working in this field have to deal with several problems associated with this type of experiment: Being especially interested in high pCO_2 scenarios, seawater carbonate chemistry needs to be adjusted and kept quasi-constant over the duration of an experiment. Also, the correct determination of at least two parameters of the carbonate system is necessary to obtain a valid description of the carbonate system and hence correctly interpret organisms' responses. Total alkalinity (A_T) and dissolved inorganic carbon (C_T) are usually favoured as input parameters for carbonate chemistry calculations, because sample preservation and measurement are relatively straightforward. pCO_2 is awkward to measure in small scale experiments, while pH has been under debate due to intricacies concerning scales and measurement protocols (Dickson, 2010; Liu et al., 2011). There is no agreement as to which two parameters are to be measured and, as a consequence, carbonate system calculations in different studies are often based on different input parameters. As will be shown here, this may severely impair comparability of different datasets.

²⁵ Even though detailed literature on measurement protocols has been published (Dickson et al., 2007; Gattuso et al., 2010), potential pitfalls and problems with uncertainty estimations remain and the quality of carbonate chemistry measurements at high pCO_2 levels is often unknown. Uncertainties of estimated pCO_2 values are generally considered to be smaller than 10 % (cf. Gattuso et al., 2010; Hydes et al., 2010). An

examination of the few over-determined datasets with carbonate chemistry measurements conducted in OA laboratories, including data from our own laboratory (reported in the supplement; Hoppe et al., 2010) reveals up to 30 % discrepancies between estimated pCO_2 levels, depending on the use of different input pairs (A_T & C_T; A_T & pH; C_T

5 & pH). This potentially widespread phenomenon has major implications on the comparability and quantitative validity of studies in the OA community. In view of the growing body of OA literature and its impact on public opinion and policy makers (Raven et al., 2005), the identification, quantification and prevention of common errors has to be an issue of high priority. The present publication is based on an earlier manuscript entitled

10 "On CO_2 perturbation experiments: Over-determination of carbonate chemistry reveals inconsistencies" (Hoppe et al., 2010).

2   Results

We present here a comparison of over-determined, OA-community based carbonate chemistry datasets found in the literature together with our own datasets. Only

15 one dataset with more than two measured parameters of the carbonate system was found in the list of "EPOCA relevant publications" archived in the PANGEA[®] database (http://www.epoca-project.eu/index.php/data.html; Nisumaa et al., 2010): Schneider and Erez (2006; doi:10.4319/lo.2006.51.3.1284). Another study was excluded from this analysis because of conflicting values between database and manuscript. In ad-

20 dition, the data from Iglesias-Rodríguez et al. (2008; doi:10.1126/science.1154122), Thomsen et al. (2010; doi:10.5194/bg-107-3879-2010) and our own laboratory (Hoppe et al., 2010; supplement) are shown. For all datasets, values reported for relevant parameters (e.g. salinity, temperature, pH scale etc.) and the dissociation constants of carbonic acid of Mehrbach et al. (1973; as refit by Dickson and Millero, 1987) were

25 used to calculate pCO_2 values at 15 °C using the program CO_2sys (Pierrot et al., 2006). If relevant data were not reported, values were estimated from other sources (e.g. for the dataset of Schneider and Erez, 2006, phosphate and silicate concentrations for the Gulf of Eilat were taken from Mackey et al., 2009).

These calculations revealed discrepancies in the pCO_2 calculated from different input pairs which increased systematically with increasing pCO_2 (Fig. 1). The pCO_2 calculated from C_T and A_T was $\sim 30\,\%$ lower than the pCO_2 calculated from either C_T and pH, or from A_T and pH, the latter pairs yielding comparable results (Fig. 1).
5 The carbonate system of Iglesias-Rodríguez et al. (2008; as shown in the PANGEA[®] database) was not strictly over-determined. However, if one assumes equilibration of the aerated seawater with the gas mixtures used (280–750 ppm), the deviation of the pCO_2 values calculated from A_T and C_T from the target pCO_2 reveals a similar relationship to that observed in the other datasets (Fig. 1).
10 With respect to our own dataset, further information is available in the auxiliary materials. Calculated pCO_2 values based on C_T and pH, or A_T and pH, compare reasonably well with the values expected from the gas mixtures used for aeration (180 ± 10 and 1000 ± 20 ppm CO_2) as well as with CO_2 concentrations determined by means of membrane-inlet mass spectrometry (MIMS). In contrast, the pCO_2 calculated from C_T
15 and A_T was up to $\sim 30\,\%$ lower. This discrepancy was observed whether C_T or A_T was manipulated, and in both natural as well as artificial seawaters (NSW and ASW, respectively; auxiliary material, Table 2).

3 Discussion

Underestimation of pCO_2 calculated from measured values of A_T and C_T has been
20 described in a number of studies from the marine chemistry community, in which direct measurements of pCO_2 were compared to calculations from A_T and C_T (Lee et al., 1996; Wanninkhof et al., 1999; Lee et al., 2000; Lueker et al., 2000; Millero et al., 2002). The magnitude of these deviations is, however, much smaller than found in our study (5–10 %; cf. Lueker et al., 2000, Fig. 4). The latter datasets and those from
25 the OA community differ in the magnitude of the discrepancies (~ 5–10 % and ~ 30 %, respectively). Thus, the phenomenon observed in our study seems to be different from the one documented by marine chemists.

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Currently, we do not have an explanation for the discrepancies described here, although a few simple explanations, such as the uncertainties of dissociation constants or uncertainties attributed to A_T, C_T or pH measurements can be ruled out: Systematic errors in measured A_T (5 µmol kg^{-1}; our own data), C_T (7 µmol kg^{-1}; our own data), pH (0.02; Liu et al., 2011; Dickson, 2010) and in equilibrium constants (0.01 in pK_1^*, 0.02 in pK_2^*, Dickson, 2010) would be much too small to explain the large discrepancies in calculated pCO$_2$. The contribution of dissolved organic matter (DOM) to alkalinity has gained a lot of attention recently (Kim & Lee, 2009; Koeve et al., 2010). However, changes in A_T due to DOM cannot cause the discrepancies described here since the phenomenon was also observed in an experiment in which artificial seawater without any organic compounds or organisms growing was used (auxiliary materials, Table 2). Furthermore, experiments with nutrient-enriched North Sea seawater (our data), probably DOM-rich water from Kiel Bight (Thomsen et al., 2010) and from the oligotrophic Red Sea (Schneider and Erez, 2006) show essentially identical discrepancies (Fig. 1). Nonetheless, DOM contributions can become a significant source of error in high biomass culture studies (Kim and Lee, 2009).

It remains puzzling that these discrepancies are observed in experiments involving both A_T and C_T adjustments, different seawater compositions, as well as in several independent datasets produced with different equipment and procedures (e.g. coulometric, colourimetric and manometric C_T measurements). The fact that several independent studies carried out within the framework of ocean acidification research show similar discrepancies between calculated pCO$_2$ values (Fig. 1) suggests a systematic, as opposed to a random, deviation that will hinder a realistic judgement of the quality of datasets.

Regardless of the reasons for its occurrence, this phenomenon will have consequences for ocean acidification research. Firstly, published pCO$_2$ values may not be comparable if different input parameters were measured and used to calculate pCO$_2$. Secondly, if calculated pCO$_2$ values are underestimated by up to 30 %, an organism's respective sensitivity to acidification might be severely overestimated. This is

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especially important at pCO_2 levels $\geq 750\,\mu$atm, which are typically applied for the year 2100 scenario and therefore crucial for all CO_2 perturbation experiments. As an example one might refer to the responses of different *Emiliania huxleyi* strains to different pCO_2 levels reported by Langer et al. (2009). For strain RCC1256, the authors report strongly decreasing calcification rates above pCO_2 values of 600 µatm (the pCO_2 values of Langer et al. were derived from A_T and C_T measurements). As the study of Langer et al. (2009) was conducted in the same laboratory as this one, the presence of the discrepancies described here can be assumed. If the pCO_2 values from Langer et al. (2009) were in fact underestimated by about 25 %, our study would suggest that calcification increases until a pCO_2 of 750 µatm and only declines at values above 800 µatm. Predictions for this strain for the often proposed 2100 scenario of 750 µatm would thus differ substantially. The discrepancies in calculated pCO_2 values described here might also explain the different results in Langer et al. (2009) and Hoppe et al. (2011) with respect to the sensitivity of this strain. Thirdly, depending on the input pair chosen, the calculated carbonate ion concentration and hence the calcite and aragonite saturation states for the datasets shown here differ significantly. Discrepancies in saturation states were found to be in the range of 15–30 %.

Care must therefore be taken when comparing studies that use different pairs of input parameters. To improve comparability between future studies, it may be useful to agree on a certain pair of input parameters as long as the described discrepancies remain. We suggest, at the current time, that the OA community should use pH with A_T as input parameters when calculating the carbonate chemistry of pCO_2 perturbation experiments and, whenever possible, measure and report additional parameters. This suggestion does, however, not mean that the resulting pCO_2 values are "correct". Although choosing a particular pair of parameters provides a pragmatic approach to dealing with such discrepancies, it is unsatisfying, and – if the choice results in inaccurate calculations of pCO_2 and $[CO_3^{2-}]$ – may lead to inappropriate interpretations of the resulting observations on organisms. Currently, we neither have sufficient understanding of the uncertainties of carbonate chemistry measurements, nor a clear

demonstration that it is possible to get thermodynamically consistent data of A_T, C_T, pH and pCO_2 for seawater samples with $pCO_2 > 600\,\mu$atm (A. Dickson, personal communication). Further investigations on source and occurrence of this phenomenon are necessary. Certified reference materials (CRMs) with high pCO_2 levels, as well as calculation programs including the propagation of errors could improve estimations of uncertainties in carbonate chemistry measurements as well as calculations.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/9/1781/2012/ bgd-9-1781-2012-supplement.pdf.

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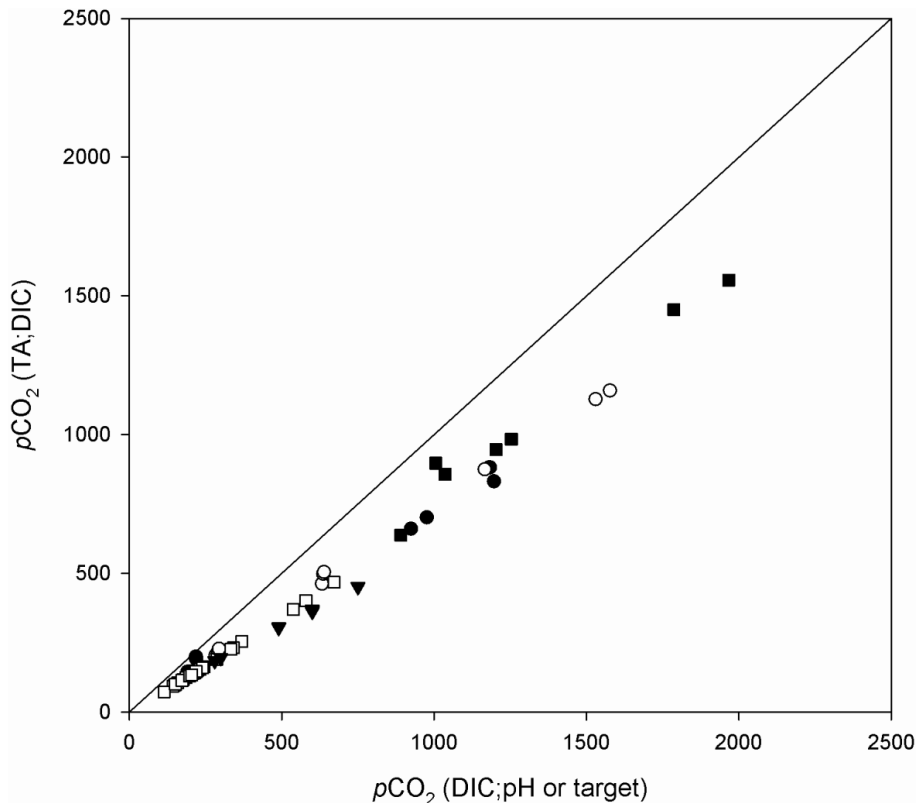15 and isotopic composition of marine plankton, Tellus, 51, 461–476, 1999.

Fig. 1. Calculated pCO_2 (A_T; C_T) versus calculated pCO_2 (C_T; pH) in µatm from this study (closed circles, natural seawater; open circles, artificial seawater), Schneider and Erez (2006, open squares), Thomsen et al. (2010, closed squares) and Iglesias-Rodríguez et al. (2008, closed triangles; here pCO_2 (target) instead of pCO_2 (C_T; pH) is given). pCO_2 values were calculated for the respective salinity, nutrient and carbonate parameter concentrations at 15 °C.