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Ocean acidification: setting the record straight

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Abstract

In recent years, ocean acidification has gained continuously increasing attention from scientists and a number of stakeholders and has raised serious concerns about its effects on marine organisms and ecosystems. With the increase in interest and the number of scientific investigations of this environmental problem, the number of opinions, often emotional, and misinterpretations of the issue have also increased. Regrettably, this is not necessarily helping to advance scientific understanding of the problem. In this article, we revisit a number of issues relevant to ocean acidification that we think require thoughtful consideration including: (1) surface seawater CO_2 chemistry in shallow water coastal areas, (2) experimental manipulation of marine systems using CO_2 gas or by acid addition, (3) net versus gross calcification and dissolution, and (4) $CaCO_3$ mineral dissolution and seawater buffering.

1 Introduction

Ocean acidification (OA), or the other CO_2 problem as it is sometimes referred to, has gained in the last several years continuously increasing attention and interest from scientists, the media, the public and policy makers. Concurrent with this increasing interest and concern for OA, research funding dedicated to the issue has significantly increased, the number of articles both in the scientific literature and popular media has exploded (cf., Gattuso and Hansson, 2011), and even several documentary movies have been produced dealing with this issue (e.g., *Acid Test*, *A Sea of Change*, *Tipping Point*, as well as others). A recent search on Google for “ocean acidification” produced 605 000 results. This is a small number compared to a search on “global warming”, which produced more than 54 million results, but nevertheless, it still clearly demonstrates increasing public interest and concern for OA. Ten years ago this search would have produced a handful of results.

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A number of pioneers between the 1960s and 1990s (e.g., Broecker et al., 1966, 1971; Bacastow and Keeling, 1973; Garrels and Mackenzie, 1981; Smith and Buddemeier, 1992; as well as others) recognized the potential problem related to increasing anthropogenic CO_2 emissions and partial absorption of the gas in the surface waters of the ocean leading to OA with effects on individual marine organisms and ecosystems. However, it was not until 1999 when Kleypas et al. (1999) published an article in *Science* titled "Geochemical consequences of increased atmospheric CO_2 on coral reefs", and then four years later when Caldeira and Wickett (2003) published an article in *Nature* titled "Anthropogenic carbon and ocean pH" that the issue gained considerable attention. At the present time, new OA research is being published in the scientific literature almost on a daily basis and reports in the popular media appear with a similar frequency. With the increasing number of investigations and interest concerning this environmental problem, the number of opinions, often emotional, and misinterpretations of this issue have also increased by both scientists and the public. Regrettably, this is not necessarily helping to advance scientific understanding of the problem. Several misconceptions have been reoccurring in the scientific literature and popular media, at scientific meetings and workshops, in manuscript and proposal reviews, and in discussions with other scientists and stakeholders that we think require some thoughtful comment and consideration. The objective of this article is to raise the awareness about some to these misconceptions and perhaps stimulate further discussion if necessary.

2 Surface seawater CO_2-carbonic acid system chemistry in shallow water coastal areas

From a forecasting perspective, OA and the associated changes in open ocean surface seawater carbonate chemistry pose little uncertainty and we can fairly accurately predict these conditions using standard CO_2-carbonic acid system chemical equations for any given scenario of anthropogenic CO_2 emissions and ocean uptake of this gas expected within the next several decades (e.g., Orr et al., 2005, 2011; Joos et al., 2011). However, it is repeatedly overlooked that in many of the shallow water coastal environments where a significant proportion of benthic calcifying organisms reside and may be at risk from OA (e.g., mussels, oysters, corals, coralline algae) that surface seawater $p\mathrm{CO}_2$ is already at levels significantly higher than expected from equilibrium with current atmospheric levels (Fig. 1). Also many large coastal ecosystems, including reefs, are found adjacent to land masses with major fluvial inputs, and hence, experience large variability in environmental parameters such as temperature, salinity, nutrient and light conditions.

The high seawater $p\mathrm{CO}_2$ and low pH conditions arise as a result of net heterotrophic conditions owing to remineralization of organic material exceeding its production, and/or in coral reef and carbonate-dominated environments from the process of calcification, which decreases seawater total alkalinity and releases CO_2. Furthermore, many of these environments undergo large diurnal fluctuations in seawater chemistry associated with daytime and nighttime changes in the intensity of photosynthesis/respiration and calcification/dissolution, as well as water advection owing to tidal cycles and changes in winds (Fig. 2). Consequently, the ambient CO_2 conditions for these environments and for the marine organisms living within them are significantly higher (or sometimes lower) than for a system currently in equilibrium with atmospheric CO_2 concentration. These conditions are rarely taken into account or even recognized in the majority of manipulation experiments with marine organisms published to date with a few exceptions.

Because upwelling and/or onwelling are important flows in coastal ocean environments, as atmospheric concentrations of CO_2 continue to rise, shallow water environments experiencing supersaturated CO_2 conditions with respect to the atmosphere potentially still could increase as the CO_2 of the open ocean source water increases. This statement assumes that net ecosystem production (NEP) and net ecosystem calcification (NEC) do not change (Mackenzie et al., 2005). Thus, in such a scenario, future surface seawater CO_2 stabilization values for many shallow coastal environments will significantly exceed the atmospheric partial pressure of CO_2. Nevertheless, increasing fluvial inputs of nutrients and organic matter to the coastal ocean (Seitzinger et al., 2010; Lerman et al., 2011) could very well alter the trophic status of this environment with subsequent changes to the seawater carbonic-acid system. This change could either exacerbate or alleviate the anthropogenic ocean acidification effect in this environment depending on the direction of the change in trophic status (Mackenzie et al., 2005). An increase in net autotrophy might alleviate the effect of anthropogenic ocean acidification by fixing more CO_2 into organic material while increasing net heterotrophy would have the opposite effect (e.g., Drupp et al., 2011). Similarly, a reduction in net ecosystem calcification owing to a decrease in Ω would act as a negative feedback to this decrease by a smaller depletion and release of total alkalinity and CO_2, respectively.

Biological feedbacks to the seawater CO_2-carbonic acid system on diurnal to seasonal timescales have been demonstrated for several coastal environments such as coral reefs and seagrass beds (Suzuki et al., 1995; Semesi et al., 2009; Bates et al., 2010), but it is obviously much more difficult to predict the biological feedback to carbonate chemistry on inter-annual to decadal timescales. Nevertheless, failure to recognize that these feedbacks exist (both positive and negative) and the fact that many coastal environments already experience CO_2 conditions significantly higher than expected from equilibrium with the atmosphere, may result in erroneous conclusions regarding the effect of OA on shallow water marine organisms and ecosystems. Similarly, CO_2 treatment values recommended at several workshops and also in the *Best Practice Guide for Ocean Acidification Research and Data Reporting* (Barry et al., 2010) are beneficial for comparisons between experiments, but it is important to recognize that these levels may not reflect present conditions or the timing of future in situ coastal seawater conditions. In our opinion these target levels should be viewed as recommendations, but not something that is set in stone and mandates all ocean acidification research. What is truly important is that researchers characterize accurately the complete dissolved inorganic carbon system including any diurnal or other temporal variability that may occur within a particular experimental system, and it is equally important to understand the current range of seawater CO_2 conditions experienced by an organism or community in the natural environment.

3 Manipulation of marine CO_2-carbonic acid system using CO_2 gas or by acid addition

In order to make predictions for the future on how marine organisms will respond to elevated seawater CO_2 conditions, one of the most logical approaches is to expose them to the anticipated future seawater conditions and record organism responses. Nonetheless, significant care and caution need to be exercised in interpreting the results of these experiments before drawing conclusions and extrapolating them to natural environments and future conditions. After all, a single species short-term CO_2 "shock" experiment in a tank with a duration of days to weeks may involve caveats in terms of its direct translation to longer-term gradual changes in CO_2 in natural environments.

Fundamentally, there are two different approaches that can be used to manipulate the seawater CO_2-carbonic acid system, i.e., addition of CO_2 gas or by addition of a strong acid or base (Schulz et al., 2009; Gattuso et al., 2010). If a seawater system is bubbled with CO_2 gas, the system will strive to reach equilibrium with the $p\mathrm{CO}_2$ of this gas phase resulting in an increase in total dissolved inorganic carbon (DIC) while total alkalinity (TA) remains unchanged with subsequent increases in $[CO_{2aq}]$, $[HCO_3^-]$ and $[H^+]$, and a decrease in $[CO_3^{2-}]$. This methodology accurately mimics the chemical changes that will occur as a result of oceanic uptake of anthropogenic CO_2 in a homogeneous gas-seawater system. In contrast, acid addition results in a decrease in the TA of the system with a subsequent change in the equilibrium between the individual components that differ slightly from the CO_2 bubbling method (see Table 1 in Schulz et al., 2009 and Table 2.1 in Gattuso et al., 2010, respectively). Recent recommendations suggest that acid manipulation experiments are accompanied, for example, by addition of $NaHCO_3$ and/or Na_2CO_3 in order to compensate for the reduction in TA (Gattuso et al., 2010), but obviously, there are many experiments conducted during the past decade that did not do this and the validity of these experiments has repeatedly come in to question.

Despite the relatively small differences in carbon speciation between acid and CO_2 manipulation experiments, opponents of the former have argued that acid addition experiments and results are not accurate in the context of OA based on the argument that they do not represent accurately changes that will occur as a result of anthropogenic OA. Technically, these opponents are correct since TA is manipulated and not the DIC with a range of resulting conditions in carbon speciation depending on whether the system is closed, open, static, or continuous-flow (Gattuso et al., 2010). In some cases these conditions will differ more than in others. For example, a static tank experiment open to the atmosphere could result in significantly different conditions as the system is allowed to equilibrate with the atmosphere and thereby loose CO_2 with a resulting decrease in DIC. This effect is insignificant in a closed or a continuous-flow system (depending on flow-rate) with very small differences in carbon speciation compared to a system bubbled with CO_2 gas. Equilibrating large volumes of seawater with CO_2 gas at a given level can be challenging and requires significant resources not available to a sufficient number of investigators. Hence, in several circumstances the acid addition method (with or without $NaHCO_3$ or Na_2CO_3 addition) has been justified and will continue to be a beneficial and a justifiable approach that could and should be used in future OA studies. In experiments where researchers are trying to mimic the natural flow regime, for example on a coral reef, with high flow rates and turnover of large volumes of water with associated replenishment of food and nutrients (e.g., Langdon and Atkinson, 2005; Kuffner et al., 2008; Jokiel et al., 2008), acid addition may logistically be a more feasible method than CO_2 bubbling for most researchers. Similarly, acid (or base) addition can be beneficial in experiments evaluating physiological processes and dependence on different carbon species (e.g., Schneider and Erez, 2006; Jury et al., 2009). Nonetheless, depending on the experimental circumstances, investigators should obviously try to mimic natural conditions as much as possible, but the fact that an experiment is conducted based on the acid addition method does not automatically reject it from being a valuable experiment.

The fundamental question at the center of the discussion is: what dissolved inorganic carbon specie(s) is/are important to marine organisms? DIC and TA are terms describing the sum of different dissolved components, which are not fixed at any given DIC or TA value, but a function of several factors including temperature, salinity, and pressure. Functionality of marine organisms probably has little to do with these terms, but is mainly controlled by the concentration and distribution of the various carbon species in the ambient seawater, the concentration gradients between the external seawater environment and the calcifying fluid and its carbon species distribution and/or the availability of H^+, CO_{2aq}, HCO_3^- or CO_3^{2-}, which are important for a marine organism's metabolic processes such as photosynthesis and calcification (Raven, 1993; Gattuso et al. 1999; Cohen and McConnaughey, 2003; Allemand et al., 2011). Some researchers have argued that small differences on the order of a few percent in $[HCO_3^-]$ between acid addition and CO_2 bubbling may explain contradictory responses in experimental results (e.g., Iglesias-Rodriguez et al., 2008). This is perhaps the case for some organisms, but to make robust and valid conclusions, direct side-by-side experimental comparisons are required. Few direct comparisons have been made to date, but an increasing number of researchers report similar responses resulting from acid addition and CO_2 bubbling experiments (Kurihara, 2008; Schulz et al., 2009; de Putron et al., 2011; A. Andersson, unpublished).

It is important that caution and care are exercised in interpreting experimental results based on the acid addition method, but it is similarly important to be cautious in interpreting any experimental manipulations as they are only a controlled approximation of what is happening in nature. Regardless of the method used, it is critical that researchers accurately characterize and report the complete CO_2-carbonic acid system parameters as well as other important parameters in their experiments, like nutrient concentrations.

4 Net versus gross calcification and dissolution

A large number of OA experiments to date have been conducted on corals (Gattuso and Hansson, 2011). So far the results have been relatively consistent demonstrating that the rate of calcification decreases as a result of decreasing seawater carbonate saturation state (cf., reviews in Langdon and Atkinson, 2005; Erez et al., 2011; Andersson et al., 2011). Similarly, experiments or observational studies of subtropical and tropical calcifying communities have shown similar results with decreasing net community calcification as a function of decreasing seawater carbonate saturation state (e.g., Langdon et al., 2000, 2003; Yates and Halley, 2003, 2006; Silverman et al., 2007; Andersson et al., 2009). In many cases these results are based on the alkalinity anomaly technique (Smith and Key, 1975; Smith and Kinsey, 1978; Chisholm and Gattuso, 1991) and the assumption that for every mole of $CaCO_3$ precipitated or dissolved, seawater total alkalinity changes by two moles. Although processes other than calcification and dissolution, such as nutrient uptake and release, ammonia and sulfate reduction, may influence total alkalinity, these processes have a relatively minor effect in most coral reef environments relative to the influence of calcification and dissolution processes. Nevertheless, there could be exceptions to this assumption that need to be carefully considered especially in natural or experimental settings where nutrient and/or organic acid concentrations are high (Dickson, 2010).

A bigger problem arises from the fact that researchers repeatedly overlook that the alkalinity anomaly technique is only measuring the net effect of calcification and dissolution, and does not distinguish between these two processes (Langdon et al., 2010). This may not be much of a problem in evaluating the response of individual organisms to OA, but for calcifying communities and ecosystems it may have greater implications. For example, a decrease in net community calcification could result from a decrease in gross calcification or an increase in gross dissolution, or a combination of both of these effects. At this time we do not know which process is more sensitive or if they are equally sensitive in most ecosystems and how they will change in response to

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OA. The effect of OA on $CaCO_3$ dissolution has been given very little attention despite the fact that almost all the reported results represent the net effect of calcification and dissolution. Attempts have been made to evaluate the problem based on observations of nighttime dissolution and from environments where calcification is believed to be non-existent or minimal (e.g., Silverman et al., 2007; Andersson et al., 2007), but these estimates are nevertheless still net estimates. Although surface seawater in most ocean regions is supersaturated with respect to the major carbonate phases present in sediments and reef framework, dissolution is an ongoing process and occurs in all these regions. The dissolution process is either driven by microbial decomposition of organic material (i.e., metabolic dissolution) that creates undersaturated conditions in sediment pore waters or microenvironments, or by bioeroding organisms that actively penetrate carbonate substrates by various acidification mechanisms. Some of these bioeroders are photosynthesizing (e.g., endoliths), and hence, may be more efficient at penetrating carbonate material and contributing to dissolution during daytime (Tribollet et al., 2006; Tribollet, 2008). The problem at hand is similar to the problem of quantifying gross primary production and respiration and their relative contribution to net primary production. However, an important difference is that photosynthesis primarily occurs when sufficient light is available (i.e., PAR, Photosynthetitically Available Radiation) while both calcification and dissolution can take place at all times. Perhaps some cleverly designed experiments based on isotope addition or some other traceable parameter (e.g., strontium enrichment) could be used to address this problem. Understanding the relative contribution from gross calcification and dissolution to net ecosystem calcification and the processes controlling their magnitude would significantly improve our ability to predict future consequences of OA, for example, on $CaCO_3$ accretion on coral reefs. Until this can be accomplished, it is important to recognize that the alkalinity anomaly technique is measuring the net effect of calcification and dissolution. Nonetheless, the effects of OA on calcification and dissolution rates are but one concern associated with this major change in seawater chemistry, and there are many other aspects important to an organism's and/or ecosystem's success that also need to be considered (e.g., fecundity, recruitment, early development, metabolism, predator-prey interactions, and community structure).

5 $CaCO_3$ mineral dissolution and seawater buffering

Following the article by Kleypas et al. (1999) on the "Geochemical consequences of increased atmospheric CO_2 on coral reefs", a couple of abstracts appeared in the *Proceedings from the 9th International Coral Reef Symposium* in Bali proposing that rising CO_2 would not greatly impact reef systems since any reduction in pH would be rapidly compensated for by dissolution of high magnesian calcite minerals (Barnes and Cuff, 2000; Halley and Yates, 2000). This was followed by a lively discussion online on the coral-list (http://coral.aoml.noaa.gov/archive/coral-list-2001.txt) between several individuals arguing whether or not this process, referred to as the magnesian salvation theory (MST), was important. The idea behind the hypothesis arose from the fact that shallow water carbonate sediments contain a significant proportion of abiotic cement and mainly skeletal Mg-calcite minerals (~25 %; Land, 1967; Morse and Mackenzie, 1990). Mg-calcite mineral phases are mainly produced by marine calcifiers such as certain algae, benthic forams, echinoderms, and bryozoans. Mg-calcite is a variety of calcite in which a significant proportion of calcium ions (up to 30 %) has been randomly replaced in the mineral structure by smaller magnesium ions causing distortions to the ideal $CaCO_3$ calcite mineral structure. As a result of this distortion and also because of inclusion of other impurities, such as HCO_3^-, OH^-, H_2O, and SO_4^{2-}, Mg-calcite minerals with significant magnesium content are more soluble than both calcite and aragonite, the latter being the mineral phase deposited by corals. As seawater CO_2 continuously increases and the saturation state with respect to carbonate minerals decreases, Mg-calcite phases will be the first mineral phases subject to undersaturated conditions and most likely subject to dissolution, "the canary in a coal mine" of OA (Mackenzie et al., 1983; Morse et al., 2006; Andersson et al., 2008; see also Walter and Morse, 1985, on the complexities tied to this statement in terms of dissolution rates of biogenic phases).

Dissolution of carbonate minerals consumes CO_2 and produces total alkalinity:

$$CO_2 + H_2O + Ca_{(1-x)}Mg_xCO_3 = (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- \quad (1)$$

As a result, the pH and saturation state with respect to carbonate minerals increases. Hence, the dissolution process potentially can act as a buffer counteracting the modifications in seawater carbon chemistry imposed by uptake of anthropogenic CO_2. If carbonate dissolution were able to keep up with the uptake of anthropogenic CO_2, the seawater would be significantly buffered and its pH would remain unchanged (Fig. 3). In summation, the MST suggests that undersaturated conditions and dissolution of highly soluble Mg-calcite phases as a result of OA will buffer the CO_2-carbonic acid system of seawater and prevent any negative effects on marine organisms.

During the ongoing discussion on the coral-list about the MST, Dr. Bob Buddemeier commendably outlined why dissolution of high Mg-calcite would not significantly buffer seawater from OA (http://coral.aoml.noaa.gov/archive/coral-list-2001.txt). This fact had also been pointed out previously in a US Department of Energy report edited by Garrels and Mackenzie (1981). Later, Andersson and colleagues (Andersson et al., 2003, 2005, 2006, 2007; Morse et al., 2006) showed in a number of papers based on a numerical modeling approach that the global coastal ocean, as well as most shallow water environments in general, will not be significantly buffered by dissolution of carbonate minerals on time-scales of decades to hundreds of years. However, these authors have failed to convince skeptics as the issue is continuously being raised or mentioned in a number of forums and settings without due consideration of what is required to achieve a significant buffer effect (e.g., Loáiciga, 2006; Tribollet et al., 2009; Hauck et al., 2011). The first step that needs to be recognized is that evidence of dissolution of $CaCO_3$ does not automatically mean that a significant buffer effect can be achieved. On time-scales of several thousands of years, dissolution of carbonate sediments in both shallow coastal waters and most importantly at depth in the ocean attendant by the consequent shoaling of the saturation horizon will act as the ultimate sink of anthropogenic CO_2, the antacid or buffer effect of the world ocean (Archer et al., 1998; Broecker, 2003), a process mainly dictated by the overturn rate of the ocean, which

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is on the order of roughly 1000 years. So why is it the case that dissolution of shallow water carbonate sediments will not significantly buffer the carbon system of ocean surface waters on the time-scale of decades to centuries?

The first question we might ask is whether there is enough shallow water reactive high Mg-calcite material available to buffer the surface ocean? There is roughly 10.4×10^{15} mol, or 125 Pg, of carbon as Mg-calcite available for this reaction (Garrels and Mackenzie, 1981; Andersson et al., 2003, 2005). From a stoichiometric standpoint, assuming that the oceanic uptake of 1 mol of CO_2 will be balanced by dissolution of 1 mol of Mg-calcite, this process going to completion could proceed for about 60 yr at an absorption rate of surface seawater of $\sim 2\,\mathrm{Pg\,C\,yr^{-1}}$ (Le Quéré et al., 2009; Takahashi et al., 2009) before the entire reactive Mg-calcite reservoir was fully exhausted. Nonetheless, to maintain a constant seawater pH, less than 1 mol of $CaCO_3$ is required for every mol of CO_2 absorbed. Thus, there appears at first glance to be a sufficient mass of reactive Mg-calcite to produce an important buffer effect at this uptake rate for the next several decades. If aragonite dissolving in shallow pore waters were also taken into consideration, even more reactive $CaCO_3$ would be available (see E. Sundquist for a different opinion in Garrels and Mackenzie, 1981). However, one must keep in mind that most of the anthropogenic CO_2 absorbed by the oceans is taken up in the open ocean and is not available for dissolution of shallow-water carbonate phases unless the acidified water is upwelled and/or onwelled into coastal waters.

Second, we might inquire whether or not anthropogenic emissions of CO_2 will change surface seawater carbon chemistry sufficiently so that seawater will become undersaturated with respect to the average Mg-calcite composition and consequently subject to dissolution? Under current CO_2 emission scenarios, it is highly likely that surface seawater at high latitudes will become undersaturated with respect to aragonite within the present or early part of the next century (e.g., Orr et al., 2005; 2011). Consequently, for Mg-calcite phases more soluble than aragonite (i.e., phases with more than 8 to 12 mol % $MgCO_3$), seawater will be undersaturated with respect to these phases and potentially subject to dissolution (as discussed below, this is also a kinetic

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problem) prior to this condition. At intermediate and low latitudes, this question is more difficult to answer because there are currently two different solubility curves for Mg-calcite minerals and we do not know which one best represents what is going on in the natural environment (e.g., Plummer and Mackenzie, 1974; Bischoff et al., 1993; Morse et al., 2006; Andersson et al., 2008). If we accept the more conservative solubility curve of Bischoff et al. (1993), surface seawater will remain supersaturated in tropical and temperate latitudes even with respect to a calcite mineral phase containing 18 mol % $MgCO_3$ by the end of this century under a BAU CO_2 emission scenario (Andersson et al., 2008). In contrast, based on the higher solubility estimate of Plummer and Mackenzie (1974), surface seawater in tropical and subtropical latitudes is at present time close to a metastable equilibrium with respect to a Mg-calcite composition containing 15 mol % $MgCO_3$. Shallow water carbonate sediments have an average Mg-calcite composition of approximately 13 to 15 mol % $MgCO_3$ (Morse and Mackenzie, 1990). Thus, as the ocean becomes more acidic, its surface waters could become undersaturated with respect to the majority of shallow water Mg-calcite phases. These phases then would be subject to dissolution if the higher solubility estimate of Plummer and Mackenzie (1974) most accurately describes the behavior of Mg-calcite phases in the natural environment. Nevertheless, even if a mineral phase is subject to dissolution, the rate of dissolution (i.e., the kinetics of the reaction) needs to be sufficiently fast relative to the rate of ocean uptake of CO_2 (or CO_2 production from organic matter decomposition), as well as the rate of physical exchange of seawater between the open ocean and shallow water environments, in order to produce a significant buffer effect. The rate of dissolution is not strictly controlled by solubility. For instance, biogenic Mg-calcite minerals of less solubility may dissolve faster than those of greater solubility because of grain microstructural complexity. In other words, this complexity may override thermodynamic constraints resulting in the dissolution of a thermodynamically more stable biogenic mineral phase (Walter and Morse, 1985). Nevertheless, net $CaCO_3$ dissolution rates in the natural environment are in general slow relative to rates of increasing CO_2 (see Table 3 in Andersson et al., 2007).

The buffering question primarily boils down to a simple mass balance problem where the rate of dissolution needs to be fast enough in order for total alkalinity to accumulate and thus buffer the CO_2-carbonic acid system. Figure 3 illustrates two hypothetical scenarios of (a) no buffering from $CaCO_3$ dissolution, i.e., no change in total alkalinity, and (b) sufficient buffering and accumulation of total alkalinity in order to maintain a constant seawater pH. The figure demonstrates that by evaluating the total alkalinity balance of a system, it can be determined whether the system is buffered or not from $CaCO_3$ dissolution. However, it is important to keep in mind that evidence of $CaCO_3$ dissolution does not mean that the system is sufficiently buffered to prevent negative effects on marine organisms. Previous exclamations of a significant buffer effect on human relevant timescales repeatedly overlook the importance of physical mixing (Barnes and Cuff, 2000; Halley and Yates, 2000). The area of the open ocean involved in the uptake of anthropogenic CO_2 is very large compared to the area of shallow water $CaCO_3$ sediments that potentially could neutralize this CO_2. In general, the flushing of these shallow $CaCO_3$ rich environments with open ocean water is too fast for any significant accumulation of alkalinity within these environments.

One example of a system that experiences accumulation of total alkalinity owing to carbonate mineral dissolution is Devil's Hole, Harrington Sound, Bermuda (Andersson et al., 2007). In summer, a seasonal thermocline develops and separates the mixed layer from the subthermocline layer at this site (Fig. 4). Organic matter remineralized in the subthermocline layer produces CO_2 that causes a reduction in seawater pH and saturation state with respect to carbonate minerals, which begin to dissolve. Metastable Mg-calcite minerals make up a significant proportion of the sediments in Devil's Hole and Harrington Sound (Neumann, 1965; Andersson et al., 2007). Evidence of dissolution can be seen from an increase in total alkalinity and calcium concentrations, which accumulate within the subthermocline layer (Fig. 5). This is also evidence that the system is experiencing a buffer effect. Nevertheless, despite evidence of dissolution of high Mg-calcite minerals and accumulation of alkalinity in Devil's Hole in response to elevated CO_2, the seawater pH and aragonite saturation state levels are sufficiently low to affect negatively most shallow water marine calcifiers.

In conclusion, at present time and for most shallow water environments, the rate of CO_2 uptake and the rate of physical mixing are too fast relative to the rates of dissolution of Mg-calcite phases in order for sufficient alkalinity to accumulate and buffer the carbon system of coastal ocean ecosystems, including regional coral reef systems.

6 Concluding remarks

In this article we have addressed four topics relevant to ocean acidification research that in our opinion have been associated with several misconceptions that we have encountered in various forums including the scientific literature, conference proceedings, manuscript and proposal reviews, as well as in discussions with fellow scientists. Our intention with this article is to raise the awareness of the community of these misconceptions and stimulate further necessary discussion. In the following, we summarize some of the key points and propose some potential future research avenues and practices to consider including:

- For any ocean acidification experiment involving organisms from near-shore environments, what is the natural range and variability of CO_2 conditions experienced by these organisms? In many cases, ambient CO_2 conditions are significantly higher than anticipated for equilibrium with the atmosphere. Hence, it is important to quantify variability (i.e., minimum, maximum and mean) in seawater chemistry in both the natural environment and in experimental setups. It is absolutely critical that the complete CO_2-carbonic acid system (i.e., H^+, CO_2, HCO_3^-, CO_3^{2-}, DIC, TA) be fully characterized. Obviously, it is similarly important to characterize other relevant environmental parameters such as temperature, salinity, nutrient, and light conditions.

- It is not justified to discard acid (or base) manipulation experiments simply because these experiments do not exactly mimic the process of anthropogenic ocean acidification. There may be other advantages provided by these experiments that carefully need to be considered. Nevertheless, additional direct side-by-side comparison of acid and CO_2 addition experiments are required to put this discussion to rest. This could also settle some enduring disagreements regarding contradictory results that have been attributed to acid versus CO_2 gas treatment.

- It is important to recognize that the alkalinity anomaly technique is measuring the net effect of gross calcification and dissolution. To predict accurately the effect of OA, for example, on coral reef communities, it is beneficial to be able to quantify these processes independently. What are the major controls of gross calcification and dissolution, and how do they change in response to rising seawater CO_2 and decreasing Ω?
- It is well established that $CaCO_3$ will dissolve in response to high CO_2 and low pH once an equilibrium threshold has been surpassed. For aragonite and calcite, these thresholds are relatively well known in seawater, but for biogenic Mg-calcite minerals they are still uncertain in the natural environment. What are these thresholds, what are the controls, and most importantly what are the controlling factors in the dissolution kinetics of the reactions involving these mineral phases?
- Any attempts to address whether dissolution of $CaCO_3$ will significantly buffer seawater of a particular system (small or large) need to consider the following questions:
  - (1) What evidence is there of a buffer effect? Observations of dissolution alone do not automatically mean that a significant buffer effect is produced.
  - (2) What are the kinetics of dissolution, i.e., the mechanisms and rates of the reactions?
  - (3) What is the physical mixing/hydrographic regime? Accumulation of total alkalinity in static experimental vessels has little relevance to most of the natural environment, which is well flushed.

Based on the current global socio-economic and political situation, it is highly unlikely that there will be a significant reduction or slow-down in CO_2 emissions during the next several decades. Thus, we can with a very high degree of certainty conclude that the atmospheric concentration of CO_2 will continue to increase and as a result the acid-base balance of surface seawater will also continue to change. There is no doubt that this major change in seawater carbon chemistry is of great concern in terms of how it will affect individual marine organisms and ecosystems. It is critical that scientists remain objective about this issue and provide objective statements and advice regarding the potential consequences of ocean acidification. The potential threat to individual organisms and organism communities and to ecosystem services and resources that will arise from OA are very serious, but it is important to not exaggerate and provide sensational statements that are misleading and not substantiated by the currently available scientific data. In the long term, this may damage the credibility of scientists and their ability to influence public and political stakeholders to make educated science-based decisions regarding CO_2 emissions, climate and the issue of OA. Unfortunately, the tendency of the popular media to focus on sensational news has become increasingly apparent in science as well. In the scientific literature, and especially in some of the journals with the highest impact factor, we feel that an increasing number of articles with sensational statements and/or far-fetched extrapolations, but with little or weak information about the details of the actual research and science, have appeared with increasing frequency. Interestingly, it is these statements or extrapolations that the popular media commonly pick-up on and reveal to the general public.

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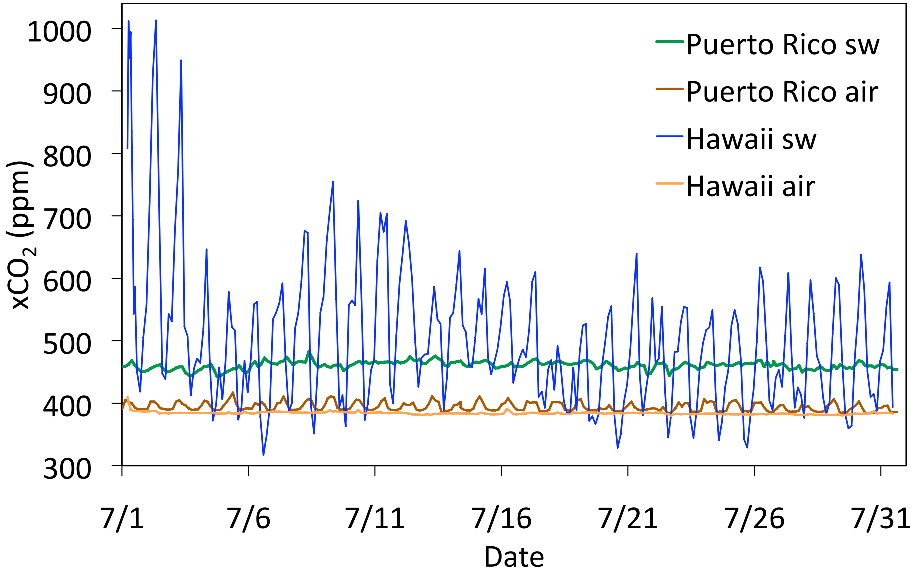

Fig. 1. Air and surface seawater xCO_2 (ppm) from two near-shore environments in Hawaii and Puerto Rico during summer of 2008 and 2009, respectively, showing xCO_2 levels that on average are significantly higher than expected from equilibrium with the atmosphere. On occasion xCO_2 levels at the Hawaii site have been observed to exceed 1000 ppm, which is much higher than the levels predicted to occur in the atmosphere in the year 2100 under a business-as-usual CO_2 emission scenario. Data courtesy: Eric DeCarlo, University of Hawaii, Dwight Gledhill, NOAA AOML, and Chris Sabine, NOAA PMEL. http://www.pmel.noaa.gov/co2/story/Coral+Reef+Moorings.

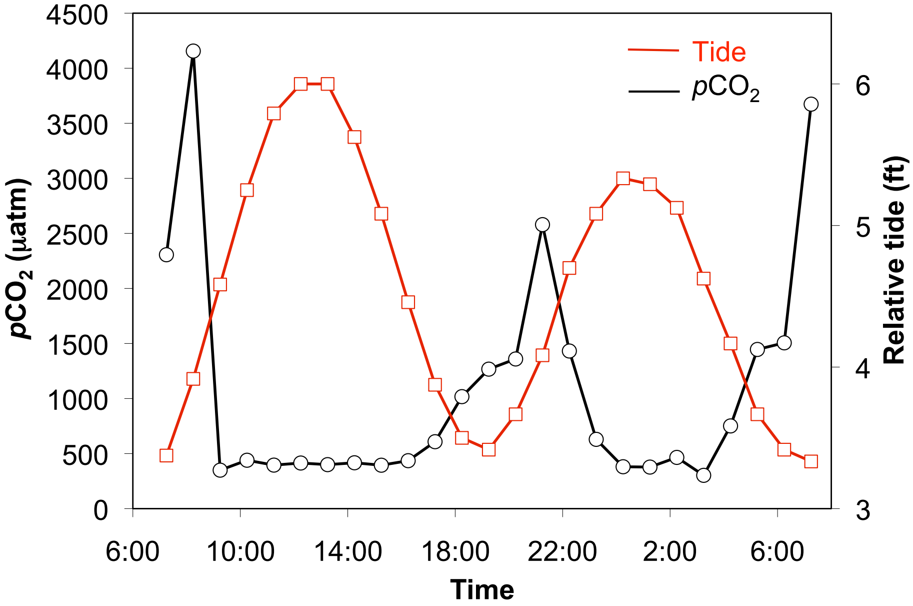

Fig. 2. Example of a near-shore mangrove environment in Bermuda, which undergoes large diurnal fluctuations in seawater carbonate chemistry over diurnal cycles owing to tidal flushing (and pumping) and groundwater intrusion as well as changes in ecosystem metabolism (e.g., photosynthesis, respiration, calcification, and $CaCO_3$ dissolution) between night and day. Surface seawater pCO$_2$ (black line) and relative tide (red line) over a 24 h period are shown.

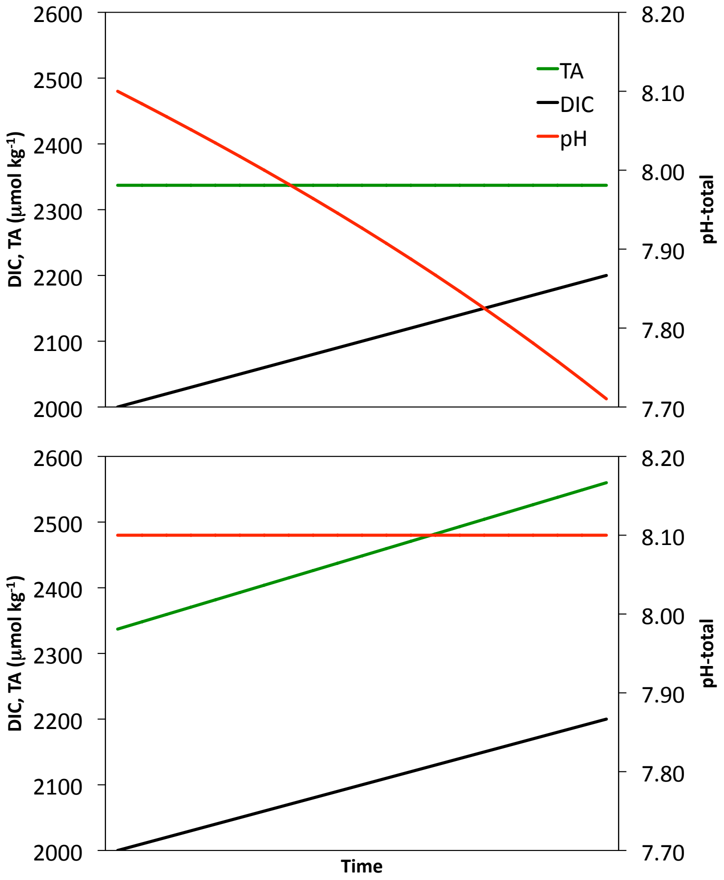

Fig. 3. Hypothetical illustration of a system that receives no buffering (top panel) from dissolution of $CaCO_3$ minerals, i.e., seawater total alkalinity remains unchanged, and a system that is buffered by $CaCO_3$ dissolution (bottom panel) in order to maintain a constant pH, i.e., total alkalinity increases and accumulates within the system.

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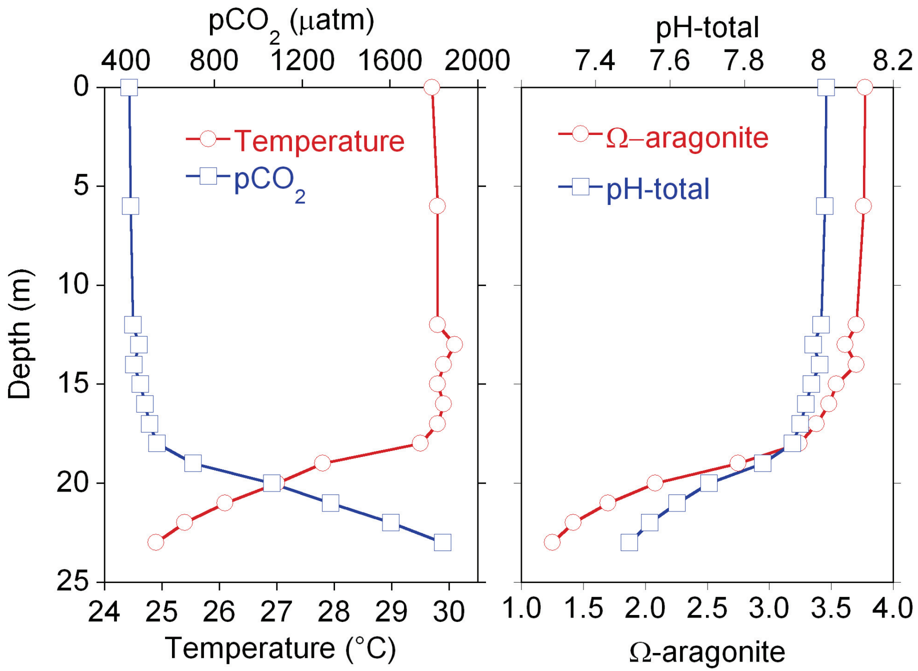

Fig. 4. Summertime vertical profiles from Devil's Hole, Bermuda, showing temperature and $p\mathrm{CO}_2$ (left panel), and aragonite saturation state (Ω) and pH-total (right panel). Due to the thermal stratification of the water column, CO_2 produced from microbial decomposition of organic material accumulates within the subthermocline, producing low Ω-aragonite and pH.

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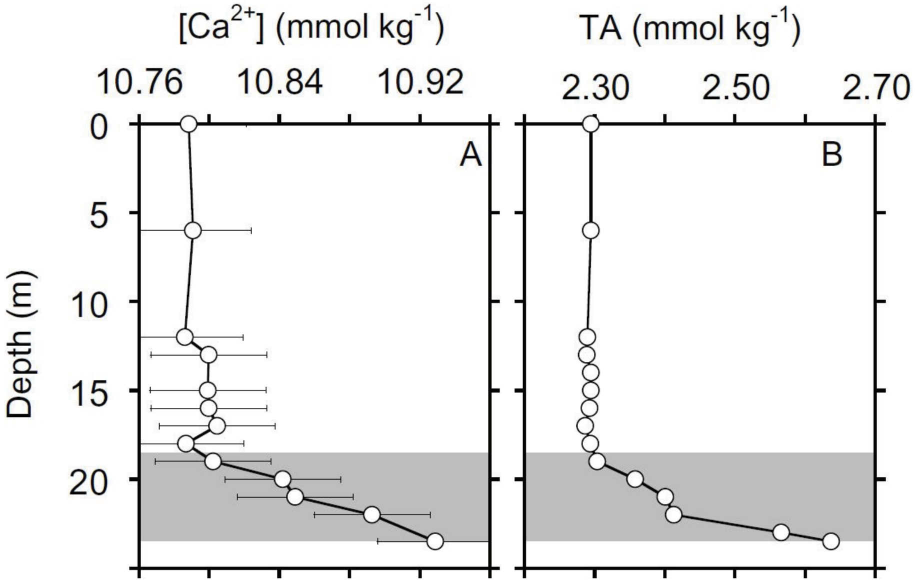

Fig. 5. Vertical profiles of **(A)** [Ca^{2+}] and **(B)** TA in Devil's Hole, Bermuda. The increase of both parameters in the subthermocline layer (gray shaded area) indicates $CaCO_3$ dissolution in the water column and surface sediments of biogenic Mg calcite phases. Despite significant dissolution and buffering, Ω-aragonite and pH remain at low levels.