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Food for Thought

Climate sensitivity and the rate of ocean acidification: future impacts, and implications for experimental design

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The global mean surface temperature and partial pressure of carbon dioxide (CO_2) are increasing both in the atmosphere and ocean. Oceanic CO_2 uptake causes a decline in pH called ocean acidification (OA), which also alters other biologically important carbonate system variables such as carbonate mineral saturation states. Here, we discuss how a "temperature buffering" effect chemically links the rates of warming and OA at a more fundamental level than is often appreciated, meaning that seawater warming could mitigate some of the adverse biological impacts of OA. In a global mean sense, the rate of warming relative to the CO_2 increase can be quantified by the climate sensitivity (CS), the exact value of which is uncertain. It may initially appear that a greater CS would therefore reduce the negative influence of OA. However, the dependence of the rate of CO_2 increase on the CS could enhance, nullify or even reverse the temperature buffering effect, depending upon the future trajectory of anthropogenic CO_2 emissions. Regional deviations from the global mean seawater temperature and CO_2 uptake trends could modulate local responses to OA. For example, mitigation of OA impacts through temperature buffering could be particularly effective in the Arctic Ocean, where the surface seawater warming rate is greater than the global mean, and the aqueous CO_2 concentration might increase more slowly than elsewhere. Some carbonate system variables are more strongly affected than others, highlighting the need to develop a mechanistic understanding of precisely which variables are important to each biogeochemical process. Temperature buffering of the marine carbonate system should be taken into account when designing experiments to determine marine species and ecosystem responses to warming and OA, in order that their results accurately reflect future conditions, and therefore can generate realistic predictions when applied to Earth system models.

Keywords: aragonite, calcification, carbon dioxide, climate change, climate sensitivity, marine carbonate chemistry, ocean acidification, saturation state, temperature.

Introduction

The partial pressure of carbon dioxide in the atmosphere (pCO_2) is currently increasing due to anthropogenic CO_2 emissions and land use change. Climate change is the most well-known consequence, which has regionally varied impacts, along with an increase in the Earth's global mean surface temperature (IPCC, 2013). About a quarter of each year's CO_2 emissions dissolve into the oceans (Le Quéré *et al.*, 2009), where they react to decrease the oceanic pH in a process commonly known as ocean acidification (OA) (Gattuso and Hansson, 2011). Although this oceanic CO_2 uptake is beneficial from a climatic perspective, OA may have consequences of its own for marine species and ecosystems (Doney *et al.*, 2009), and for calcifiers in particular. Evidence from the geological record suggests that previous hyperthermal events that were accompanied by OA are often associated with declines in biogenic calcification and calcium carbonate ($CaCO_3$) preservation, along with major extinction events for marine calcifiers (Hönisch *et al.*, 2012). These past events are not perfect analogues for the present transient because their rates of change were far slower, so recent research has focussed on identifying biological responses to OA and warming in extant species (Hendriks *et al.*, 2010; Harvey *et al.*, 2013).

A wide range of approaches have been taken to better understand the effects of OA and warming (and other stressors) on biological systems. Recently there has been a drive towards multi-stressor experiments, as it has been recognised that organisms under stress from changes in one variable are likely to be less resilient to changes in another (Dupont and Pörtner, 2013; Riebesell and Gattuso, 2015). For example, a species might be able to tolerate a small change in temperature or a low level of OA, but not both together. Multi-stressor experiments may also be more appropriate as future changes in seawater chemistry and temperature will occur simultaneously.

Temperature and carbonate chemistry

An additional complication that is often overlooked is that OA is directly regulated by seawater temperature at a fundamental chemical level. After dissolving into seawater, aqueous $\mathrm{CO_2}$ ($\mathrm{CO_{2(aq)}}$) reacts to form bicarbonate ($\mathrm{HCO_3}^-$) and carbonate ($\mathrm{CO_3^{2-}}$) ions, and releases protons ($\mathrm{H^+}$):

$$\mathrm{CO_{2(aq)}} + \mathrm{H_2O} \overset{k_1}{\rightleftharpoons} \mathrm{H^+} + \mathrm{HCO_3^-} \overset{k_2}{\rightleftharpoons} 2\mathrm{H^+} + \mathrm{CO_3^{2-}} \qquad (1)$$

These reactions continue in dynamic equilibrium, and the relative concentration of each chemical species can be determined from the equilibrium constants k_1 and k_2. These constants have been theoretically (Millero and Pierrot, 1998) and empirically (e.g. Mehrbach *et al.*, 1973) shown to be temperature-dependent. Temperature changes therefore result in shifting of these equilibria, and redistributions of the concentrations of these chemical species. This process is effectively instantaneous from an OA perspective, as the equilibration timescale for the reactions in (1) is on the order of a few seconds or faster (Eigen, 1964; Johnson, 1982).

We can perform a few simple calculations to investigate the potential consequences of this temperature dependency. First, consider a parcel of seawater that is cut off from $\mathrm{CO_2}$ exchange with the air. Warming this seawater will decrease its pH and $[\mathrm{HCO_3}^-]$ while increasing its $[\mathrm{CO_{2(aq)}}]$ and $[\mathrm{CO_3^{2-}}]$ (Figure 1; the square brackets indicate the concentration of the enclosed species in micromoles per kilogram of seawater). These changes occur entirely as a result of re-equilibration of the reactions in (1) following temperature-induced changes to k_1 and k_2. What are the consequences for OA? The answer depends on which variables are biologically important. Considering pH in isolation, it initially appears that its decline following warming constitutes an enhancement of OA. However, further investigation of other variables and an extension of the timescale for this thought experiment both suggest that we might more correctly consider it to be the opposite, in a biological context: temperature buffering of OA impacts.

It is not fully understood which variables are of direct, mechanistic importance to marine organisms, but many studies have focussed on $\mathrm{CaCO_3}$ mineral saturation states (Ω), particularly in the context of calcification (e.g. Langdon *et al.*, 2000; Riebesell *et al.*, 2000; Orr *et al.*, 2005). These can be expressed as follows:

$$\Omega = \frac{[\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]}{k_{\mathrm{sp}}} \qquad (2)$$

where k_{sp} is the "solubility product" of the $\mathrm{CaCO_3}$ mineral (usually calcite or aragonite). Returning to our simple thought experiment, the increase in $[\mathrm{CO_3^{2-}}]$ driven by warming will increase Ω, which is considered to be biologically beneficial. The k_{sp} is also a function of temperature (Mucci, 1983), but its effect on Ω is an order of magnitude smaller than that of the simultaneous temperature-driven changes in $[\mathrm{CO_3^{2-}}]$. The overall effect of warming alone is in an increase in both $\Omega_{\mathrm{aragonite}}$ and $\Omega_{\mathrm{calcite}}$, even in this hypothetical situation where there is no sea-air $\mathrm{CO_2}$ flux (Figure 1).

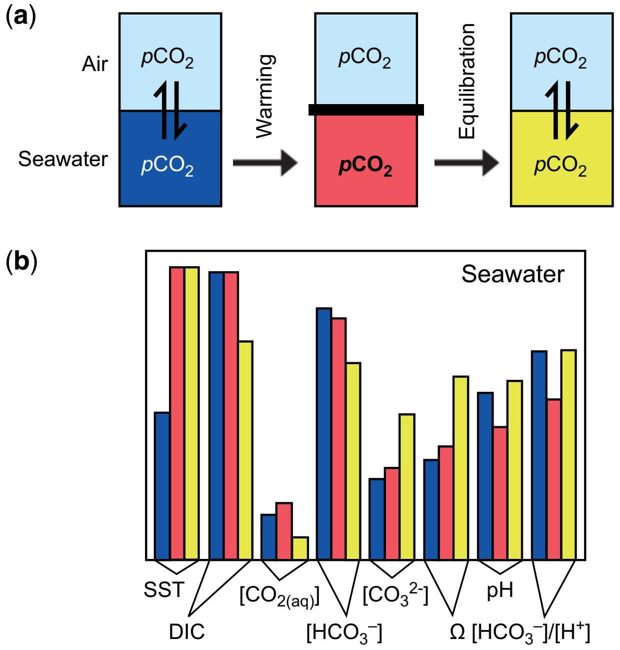

Figure 1. Schematic illustration of warming and $\mathrm{CO_2}$ equilibration thought experiments. **(a)** Initially, a parcel of seawater (left) is in equilibrium with the air. After warming, and with no air-sea $\mathrm{CO_2}$ exchange, the seawater $p\mathrm{CO_2}$ has increased (middle). The seawater then re-equilibrates back to the $p\mathrm{CO_2}$ of the air (right). **(b)** Changes in key variables during each step of the thought experiments. The colours of the bars correspond to the equivalent steps in Figure 1a. The vertical axis scale is different for each variable, and the relative sizes of the bars are schematic rather than accurate.

Of course, the assumption of zero air-sea $\mathrm{CO_2}$ flux is unlikely to hold true in the surface ocean, which is particularly important for the biological impacts of OA. As already mentioned, warming increases $[\mathrm{CO_{2(aq)}}]$ relative to the total dissolved inorganic carbon (DIC, the sum of the concentrations of $\mathrm{CO_{2(aq)}}$, $\mathrm{HCO_3}^-$ and $\mathrm{CO_3^{2-}}$). This means that after warming, the seawater $p\mathrm{CO_2}$ ($p\mathrm{CO_2^{sw}}$) is greater, which could drive a net sea-to-air $\mathrm{CO_2}$ flux. The solubility of $\mathrm{CO_2}$ is also inversely proportional to temperature (Weiss, 1974), so warming drives a further increase in the $p\mathrm{CO_2^{sw}}$ through temperature control of the equilibrium constant k_0:

$$\mathrm{CO_{2(g)}} \overset{k_0}{\rightleftharpoons} \mathrm{CO_{2(aq)}} \qquad (3)$$

This equilibrium is slower than those in (1), taking on the order of a year for a typical surface ocean mixed layer (Zeebe and Wolf-Gladrow, 2001). Nevertheless, on the multi-decadal timescale of OA we could assume that the global mean surface ocean will remain roughly in equilibrium with the atmosphere, and at a similar level of disequilibrium regionally (Takahashi *et al.*, 2009).

Extending the previous thought experiment by allowing the seawater CO_2 to re-equilibrate with a constant atmospheric value shows that the solubility effect enhances temperature buffering of the OA impact on Ω further still. In this case, warming results in a loss of DIC, and this combined with the repartitioning of the carbonate species in (1) leads to decreasing $[HCO_3^-]$ and $[CO_{2(aq)}]$, whilst pH and $[CO_3^{2-}]$ both increase (Figure 1). The $[CO_3^{2-}]$ increase is an order of magnitude greater than in the previous calculation where air-sea CO_2 exchange was restricted, so its effect on $\Omega_{\text{aragonite}}$ and Ω_{calcite} is proportionally greater (Figure 1). Seawater warming in itself therefore acts to buffer the OA impact on carbonate mineral saturation states.

In addition (or alternatively) to Ω, the ratio of $[HCO_3^-]$ to $[H^+]$ has been proposed as being of biological importance, as it quantifies the balance between a growth substrate (HCO_3^-) and an inhibitor (H^+) (e.g. Bach, 2015; Cyronak *et al.*, 2016). Applying the same thought experiments to this compound variable as we did to Ω reveals a quite different result. Warming in the absence of air-sea gas exchange results in a significant decline of $[HCO_3^-]/[H^+]$—this is OA enhancement, rather than buffering (Figure 1). Taking into account CO_2 solubility and permitting total equilibration with a constant atmosphere, we find that temperature has little influence on $[HCO_3^-]/[H^+]$ at a present-day pCO_2^{sw} of 400 µatm. The potential for temperature buffering of OA impacts on $[HCO_3^-]/[H^+]$ is much smaller than for Ω. We expect the patterns of future Ω and $[HCO_3^-]/[H^+]$ change to be different from each other (Bach, 2015), particularly in hydrographically-complex continental shelf seas (Fassbender *et al.*, 2016). This underlines the importance of establishing which variable is mechanistically more important to marine organisms in order to accurately predict their future response to OA. Either way, this uncertainty relates primarily to biological $CaCO_3$ formation; Ω is a key control on its dissolution (Morse *et al.*, 2007), so its strong temperature buffering could still be important in some contexts.

These thought experiments illustrate the possible chemical responses to warming in the two endmember situations: total and zero CO_2 equilibration with a constant atmosphere. The real-world response should fall somewhere within this range, depending upon the air-sea gas exchange rate. We do not provide exact values of the changes because they will vary depending upon local conditions [e.g. total alkalinity (TA) and salinity], but the overall patterns that we have described should be ubiquitous.

Climate sensitivity

One further interaction has been excluded from our thought experiments so far: in the real world, global mean sea surface temperature (SST) and pCO_2^{sw} are increasing together. The atmospheric pCO_2 is commonly linked to the global mean surface temperature through the concept of climate sensitivity (CS) (or response) (e.g. Otto *et al.*, 2013; Marvel *et al.*, 2016). The equilibrium climate sensitivity (ECS) is the change in the global mean near-surface air temperature resulting from a doubling of atmospheric CO_2, after the climate system has been given time to re-equilibrate. Another definition of CS that may be more relevant to the present anthropogenic CO_2 increase is the transient climate response (TCR), which is the warming that would occur after 70 years if the atmospheric CO_2 concentration rose by 1% per year throughout that period. The TCR is thought to be lower than the ECS because of the relatively slow rate of ocean heat uptake (Winton *et al.*, 2009). In either case, the higher the ECS or TCR, the greater the increase in temperature for a given increase in CO_2. Recent estimates suggest that the TCR is likely between 1.0 and 2.5 °C, while the ECS is likely in the range from 1.5 to 4.5 °C (Stocker *et al.*, 2013). Over recent decades, the rate of global mean surface pCO_2^{sw} increase has been similar to that of atmospheric pCO_2 growth (Takahashi *et al.*, 2009), while SST has increased at about 70–80% of the global mean surface temperature rate (Hartmann *et al.*, 2013). This suggests that these CS values should be decreased by 20–30% for our purposes, assuming that these trends continue into the future.

The CS framework allows us to investigate how important temperature buffering could be in a global mean sense, because a given ECS or TCR value defines a specific trajectory through SST-pCO_2^{sw} phase space. Assuming a constant TA, we can therefore calculate the future global mean state of the carbonate system as pCO_2^{sw} increases (Figure 2). For pH (Figure 2a) and $[HCO_3^-]/[H^+]$ (Figure 2b), temperature buffering is negligible at present day pCO_2^{sw}; the pH (or $[HCO_3^-]/[H^+]$) value is similar at any given pCO_2^{sw}, regardless of the CS trajectory. It increases at higher pCO_2^{sw}, although it does not become important until very high pCO_2^{sw} values are reached, predicted beyond the year 2100. For Ω, temperature buffering is apparent throughout the pCO_2^{sw} range (Figure 2c); the greater the CS, the smaller the change in Ω for a given increase in pCO_2^{sw}. In this simplistic "constant atmosphere" scenario, a greater CS could therefore be considered beneficial for mitigating the biological impacts of OA.

However, this scenario assumes that the rate of pCO_2^{sw} increase is independent of the CS, which is inaccurate. It effectively uses pCO_2 as a metric of passing time rather than time itself, but it makes more sense to assess how quickly OA-related changes might occur, rather than at what pCO_2 value they might occur. Warming of the surface ocean decreases CO_2 solubility (Weiss, 1974), thus it increases pCO_2^{sw} and reduces the net air-sea CO_2 flux. Therefore under the same CO_2 emissions scenario, more CO_2 should remain in the atmosphere when the CS is higher, so atmospheric pCO_2 (and pCO_2^{sw}) will increase faster (Figure 3). In terms of Figure 2, this means that we would move more quickly from left to right along the 5 °C trajectory than along those for lower climate sensitivities, thus opposing the temperature buffering. To approximately quantify this effect, we considered a suite of emission-driven model simulations to the year 2100 (Figure 12.36 from Collins *et al.*, 2013). These predicted a range of atmospheric pCO_2 values from about 800 to 1100 µatm, corresponding to global mean surface temperature increase of about 2.5–6.5 °C. Assuming that the highest temperature rise corresponds to the highest pCO_2 increase and equivalently for the lowest, the $\Omega_{\text{aragonite}}$ would be about 0.16 units lower in the warmer case (calculated at the same conditions used in Figure 1). For comparison, if these two endmember levels of warming occurred at a constant, intermediate pCO_2 value, then $\Omega_{\text{aragonite}}$ would be 0.24 units higher in the warmer case. In this 'constant emissions' scenario, temperature buffering of global mean Ω could therefore be overcompensated for by the faster pCO_2^{sw} increase, thus enhancing the adverse changes to the marine carbonate system.

The constant emissions scenario is more realistic than the original constant atmosphere scenario, but it still may not be an appropriate guide to the future. It assumes that the anthropogenic CO_2 emission rate is itself independent of the CS, which may not be true. Under a higher CS, temperature increases and climatic changes will occur more quickly, thus enhancing societal and political pressure to reduce CO_2 emissions. Indeed, the recent Paris

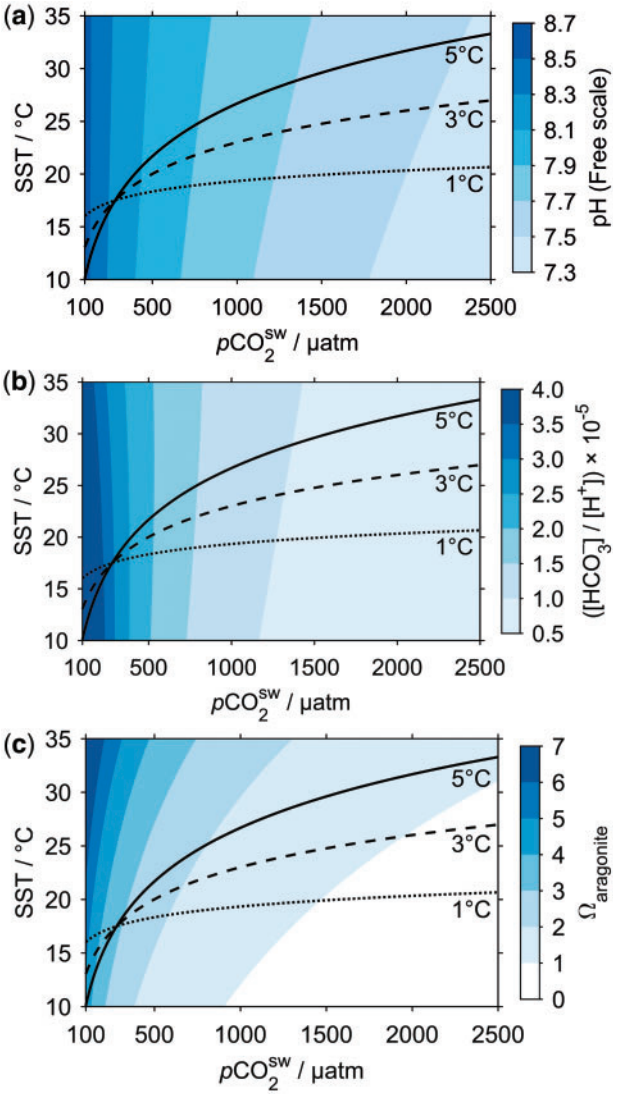

Figure 2. The relationship between SST, seawater pCO_2 and **(a)** pH, **(b)** bicarbonate ion to "proton" ratio and **(c)** aragonite saturation state. The black lines indicate the trajectories of global mean SST and pCO_2^{sw} for climate sensitivities of 1, 3 and 5 °C, beginning from preindustrial global averages of 17.5 °C and 280 µatm (Ahn *et al.*, 2012). In **(c)**, they intersect with the $\Omega_{aragonite} = 1$ contour at pCO_2^{sw} values of ~1460, 1950, and 2940 µatm, respectively (the latter is beyond the right hand edge of the plot), showing that the greater the CS, the higher that pCO_2^{sw} can rise before aragonite becomes undersaturated. All CO_2 system variables were calculated using version 1.1 of the CO_2SYS program for MATLAB (van Heuven *et al.*, 2011), with dissociation constants for carbonic acid following Lueker *et al.*, (2000) and for bisulfate following Dickson (1990), the boron:chlorinity of Lee *et al.*, (2010). The contour fields were calculated at a TA of 2250 µmol kg^{-1}, practical salinity of 35, atmospheric pressure, and zero silicate and phosphate.

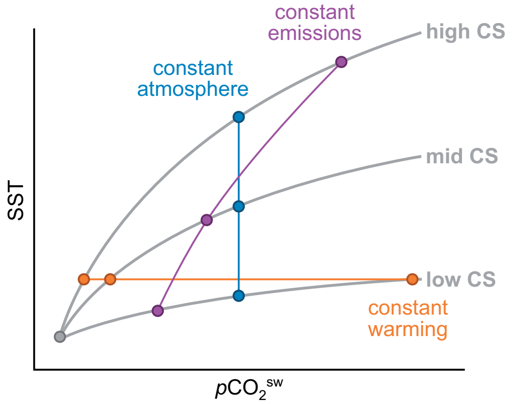

Figure 3. Schematic of total changes in SST and CO_2 partial pressure after a set amount of time from the initial condition indicated by the circle in the bottom left corner, for different CSs and future emissions scenarios: "constant atmosphere" assumes that the pCO_2^{sw} increase is independent of the CS; "constant emissions" assumes that anthropogenic CO_2 emissions will continue along a set trajectory, independent of the CS; and "constant warming" assumes that emissions are decreased in response to warming such that a set temperature threshold is not exceeded.

Agreement under the United Nations Framework Convention on Climate Change commits to limiting the global mean surface temperature increase to "well below 2 °C above pre-industrial levels". This warming threshold could be approached more quickly if the CS is greater, theoretically triggering a greater and swifter reduction in anthropogenic CO_2 emissions, and leading to a "constant warming" scenario (Figure 3). In this case, we would move more slowly from left to right along the higher CS trajectories on Figure 2. This would be beneficial for all of the variables in Figure 2, although the reduction of OA impacts is a consequence of decreased emissions, rather than being a direct effect of temperature buffering.

In summary, although a warmer temperature at a given pCO_2^{sw} will lead to a more biologically-favourable carbonate system, we cannot be certain whether a higher CS would have a chemical benefit without first knowing which path we will take on the spectrum between the constant emissions and constant warming scenarios.

Arctic Ocean

Although most oceanic regions do not have the same conditions as the global mean, the same principles still apply: the trajectory through SST-pCO_2^{sw} phase space determines the magnitude of the impact of OA. If SST and pCO_2^{sw} in any particular region follow a different trajectory to the global mean, for example due to changing circulation and currents, then that region could be said to have its own local climate response (LCR) that controls the importance of temperature buffering therein.

A key region that deviates from the global mean is the Arctic Ocean. The Arctic Ocean is presently an important sink for atmospheric CO_2, despite the limitations on air-sea gas exchange imposed by seasonal sea-ice cover (Bates and Mathis, 2009). However, it has experienced a significant decline in sea ice in recent years (Perovich and Richter-Menge, 2009; Perovich *et al.*, 2015), which has probably been mainly driven by atmospheric warming (Screen and Simmonds, 2010). The albedo reduction associated with sea-ice loss also acts as a positive feedback, further accelerating this warming (Perovich *et al.*, 2007). Significant heat fluxes into the surface ocean have also been driven by inputs of relatively warm water from the North Atlantic (Gerdes *et al.*, 2003) and turbulent vertical mixing generated by tides (Rippeth *et al.*, 2015). As a result of these processes, the Arctic Ocean has been warming faster than anywhere else on the planet, with surface SST in August 2015 reaching up to 4 °C higher than the 1982–2010 mean (Timmermans and Proshutinsky, 2015). Consequently, the LCR of the Arctic Ocean should be greater than the global TCR, as it has experienced more warming for a given increase in atmospheric $p\mathrm{CO_2}$. However, this enhanced warming is only half of the story.

Net primary production (NPP) in the Arctic Ocean rose by 30% between 1998 and 2012, partly as a result of the reduced sea ice extent (Arrigo and van Dijken, 2015), and this trend is likely to continue into the next few decades (Yool *et al.*, 2015). Indeed, 2015 saw widespread high chlorophyll-*a* anomalies across the region (Frey *et al.*, 2015). There are two ways in which this could act to further increase the Arctic LCR. First, in an extension of the well-known sea ice-albedo positive feedback (Perovich *et al.*, 2007), seawater containing high chlorophyll-*a* and biomass has increased heat absorption relative to oligotrophic seawater, so the enhanced NPP could further contribute to local warming (Park *et al.*, 2015). Second, it may also decrease $p\mathrm{CO_2^{sw}}$ through conversion of DIC into organic matter, thus increasing the LCR even more.

From a chemical perspective, these factors (enhanced warming and mitigation of the $p\mathrm{CO_2^{sw}}$ increase) both increase the localised chemical impact of temperature change. In the Arctic Ocean, the potential for temperature buffering to counteract the chemical consequences of OA could therefore be greater than the global mean, regardless of the CS.

Experimental design

Several studies have noted that OA experiments need to become more complex, moving from assessing single species responses to those of entire ecosystems, from single to multiple stressors, and from short-term acclimative to long-term adaptive responses, as well as assessing all life-cycle stages (Dupont and Pörtner, 2013; Riebesell and Gattuso, 2015). It has also been pointed out that as the surface ocean is frequently out of equilibrium with atmospheric $\mathrm{CO_2}$, it may not be appropriate to use global mean present day atmospheric $p\mathrm{CO_2}$ as a baseline for these studies, but rather to use conditions that are more relevant to the natural environment (McElhany and Busch, 2013), and to take into account natural co-variation of variables like SST and $p\mathrm{CO_2^{sw}}$ (Reum *et al.*, 2015). In addition, the interactions between carbonate chemistry and temperature discussed here should also be considered in order to design experiments that simulate realistic future ocean conditions.

For example, a single-stressor experiment that aims to change only temperature could also unintentionally affect the carbonate system, while an experiment that alters the carbonate system at constant temperature could effect greater chemical changes than are likely to occur in the real world. For the former case, consider an experimental set-up of different incubation containers that are kept at different temperatures, but all open to the same air. The $p\mathrm{CO_2^{sw}}$ would probably be similar in each container due to ongoing equilibration, so the $\Omega_{\mathrm{aragonite}}$ would be higher in the warmer containers (Figure 1). If an $\Omega_{\mathrm{aragonite}}$ decline would be detrimental to the organism in question, then any negative impact of increased temperature might be reduced somewhat by the inadvertent increase in $\Omega_{\mathrm{aragonite}}$. This could be countered by chemically manipulating the $\mathrm{CO_2}$ system to ensure constant $\Omega_{\mathrm{aragonite}}$ at the different temperature conditions, but this manipulation would have knock-on effects for other $\mathrm{CO_2}$ system variables. It is well-established that all of the $\mathrm{CO_2}$ system can be calculated if any two of its variables are known (Zeebe and Wolf-Gladrow, 2001), but this also means that only a maximum of two variables can have specific values selected as manipulation targets. It may therefore be impossible to hold all of the $\mathrm{CO_2}$ system variables that might affect biological responses constant across a range of temperature targets, rendering this possible only if the variable directly driving the biological response is known. The simplest method to ensure realistic experimental results could therefore be to increase both $p\mathrm{CO_2^{sw}}$ and temperature together in line with the anticipated LCR. Indeed, the results of a multi-stressor experiment that accurately reflected the future conditions in the region of interest could be used in a predictive capacity without needing to definitively establish which variables were mechanistically responsible for the observed biological response.

Using experimental results in models

In any Earth system model that includes greenhouse warming and an accurate representation of the marine carbonate system, temperature buffering of carbonate system variables will already be taken into account (e.g. $\Omega_{\mathrm{aragonite}}$ will automatically decrease more slowly in regions where the SST increase is higher). The important step for future experimental work is to ensure that the biological responses to OA are being measured in appropriate conditions, in order to feed into models and accurately predict global-scale responses.

For example, McNeil *et al.* (2004) used equations for the dependence of coral reef calcification on temperature (Lough and Barnes, 2000) and $\Omega_{\mathrm{aragonite}}$ (Langdon *et al.*, 2000) to predict future changes in coral reef calcification in a coupled atmosphere-ice-ocean carbon cycle model (Hirst *et al.*, 1996). These temperature- and $\Omega_{\mathrm{aragonite}}$-dependence studies effectively considered these variables in isolation, which could cause problems for the later model study. If we make the simplifying assumption that the temperature study was carried out at constant TA and $p\mathrm{CO_2^{sw}}$, then the $\Omega_{\mathrm{aragonite}}$ would not have been constant (Figure 1). The temperature range considered by Lough and Barnes (2000) was about 23–29 °C. Assuming total equilibration at a $p\mathrm{CO_2}$ of 400 µatm and a constant TA of 2250 µmol kg^{-1}, this corresponds to an increase in $\Omega_{\mathrm{aragonite}}$ of 0.63 units. Using the equation of Langdon *et al.* (2000), this increase in $\Omega_{\mathrm{aragonite}}$ should correspond to an increase in calcification rate by $\sim$26.1 mmol-$\mathrm{CaCO_3}$ m^{-2} day^{-1} (assuming that $\Omega_{\mathrm{aragonite}}$ is the actual driver of calcification rate change, rather than $[\mathrm{HCO_3}^-]/[\mathrm{CO_3^{2-}}]$). This could then be subtracted from the actual change in calcification from 23 to 29 °C observed by Lough and Barnes (2000) of 542 mmol-$\mathrm{CaCO_3}$ m^{-2} day^{-1} to arrive at the temperature-only influence. This reduces the temperature-dependence of calcification by about 5%, so McNeil *et al.* (2004) may have overestimated the warming-driven increase in calcification by this amount. This relatively small adjustment would not alter the main conclusions drawn by McNeil *et al.* (2004), but this might not be the case for other species or ecosystems that are relatively less sensitive to warming and more responsive to $\Omega_{\mathrm{aragonite}}$ changes. This uncertainty could be eliminated through proper consideration of temperature buffering during the design of single- and multi-stressor experiments.

Conclusion

There is a temperature buffering effect through which the marine carbonate system is altered in a fashion that is beneficial to biology upon seawater warming. The future rate of warming relative to atmospheric CO_2 growth—the CS—will therefore modulate the chemical changes to the marine carbonate system caused by oceanic CO_2 uptake, but the global mean consequences will depend on the pattern of future CO_2 emissions. Different carbonate system variables (e.g. $\Omega_{\text{aragonite}}$ and $[HCO_3^-]/[H^+]$) will respond differently from each other, so it is essential to further develop a mechanistic understanding of precisely which variable influences each biogeochemical process of interest. Some areas (e.g. the Arctic Ocean) are diverging significantly from the global mean warming and pCO_2^{sw} trends, causing regional variations in the capacity for temperature buffering to mitigate OA impacts. These principles should be considered when designing experiments to assess the responses of marine species and ecosystems to ongoing OA and warming, in order that the results of these experiments can be applied to model simulations and return realistic predictions.

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