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Reconsidering the role of carbonate ion concentration in calcification by marine organisms

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Abstract

Marine organisms precipitate 0.5–2.0 Gt of carbon as calcium carbonate (CaCO_3) every year with a profound impact on global biogeochemical element cycles. Biotic calcification relies on calcium ions (Ca^{2+}) and generally on bicarbonate ions (HCO_3^-) as CaCO_3 substrates and can be inhibited by high proton (H^+) concentrations. The seawater concentration of carbonate ions (CO_3^{2-}) and the CO_3^{2-} -dependent CaCO_3 saturation state (Ω_{CaCO_3}) seem to be irrelevant in this production process. Nevertheless, calcification rates and the success of calcifying organisms in the oceans often correlate surprisingly well with these two carbonate system parameters. This study addresses this dilemma through rearrangement of carbonate system equations which revealed an important proportionality between $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} and the ratio of $[\text{HCO}_3^-]$ to $[\text{H}^+]$. Due to this proportionality, calcification rates will always correlate equally well with $[\text{HCO}_3^-]/[\text{H}^+]$ as with $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} when temperature, salinity, and pressure are constant. Hence, $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} may simply be very good proxies for the control by $[\text{HCO}_3^-]/[\text{H}^+]$ where $[\text{HCO}_3^-]$ would be the inorganic carbon substrate and $[\text{H}^+]$ would function as calcification inhibitor. If the “substrate-inhibitor ratio” (i.e. $[\text{HCO}_3^-]/[\text{H}^+]$) rather than $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} controls CaCO_3 formation then some of the most common paradigms in ocean acidification research need to be reviewed. For example, the absence of a latitudinal gradient in $[\text{HCO}_3^-]/[\text{H}^+]$ in contrast to $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} could modify the common assumption that high latitudes are affected most severely by ocean acidification.

1 Introduction

Calcium carbonate (CaCO_3) is used by a large variety of marine organisms as structural material for their exo- and endoskeletons. Calcification requires calcium ions (Ca^{2+}) and dissolved inorganic carbon (DIC) substrate, which is present in seawater

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ter as carbon dioxide (CO_2), bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}). From a purely chemical point of view, calcium reacts with inorganic carbon as:



Precipitation is thermodynamically favored when $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ reach or exceed the solubility of CaCO_3 in seawater. The stoichiometric solubility product is defined as:

$$K_{\text{sp}}^* = [\text{Ca}^{2+}]_{\text{saturated}} [\text{CO}_3^{2-}]_{\text{saturated}} \quad (2)$$

and is a function of temperature, salinity, and pressure (Mucci, 1983; Zeebe and Wolf-Gladrow, 2001). The saturation state of CaCO_3 (Ω_{CaCO_3}) is calculated with seawater concentrations of Ca^{2+} and CO_3^{2-} and K_{sp}^* as:

$$\Omega_{\text{CaCO}_3} = \frac{[\text{Ca}^{2+}]_{\text{seawater}} [\text{CO}_3^{2-}]_{\text{seawater}}}{K_{\text{sp}}^*} \quad (3)$$

Accordingly, CaCO_3 precipitation is thermodynamically favored when the product of $[\text{Ca}^{2+}]_{\text{seawater}}$ and $[\text{CO}_3^{2-}]_{\text{seawater}}$ reaches or exceeds K_{sp}^* or $\Omega_{\text{CaCO}_3} \geq 1$. In the oceans, Ω_{CaCO_3} is largely determined by $[\text{CO}_3^{2-}]$ because $[\text{Ca}^{2+}]$ is rather constant in seawater (Kleypas et al., 1999).

Biogenic CaCO_3 is mainly present as calcite or aragonite, which have different crystal structures and solubility. Calcite is predominantly formed by coccolithophores, foraminifera, and some crustaceans while aragonite is typically found in scleractinian corals. Molluscs can have both, calcite and aragonite. Echinoderms and octocorals build calcite with a large fraction of magnesium (Mg) included in the crystal lattice (Mann, 2001). Aragonite is more soluble than calcite which is expressed in an offset between their individual K_{sp}^* values (Mucci, 1983). This offset, however, is the only major difference in their solubility and changes in $\Omega_{\text{aragonite}}$ are very similar to changes in

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Ω_{calcite} (Zeebe and Wolf-Gladrow, 2001). They are therefore summarized in the term Ω_{CaCO_3} in this study since changes in the saturation state rather than absolute numbers are addressed here.

On the biological level, chemical precipitation of CaCO_3 as defined in Eq. (1) is just the final step in the calcification process. Before precipitation, calcium and inorganic have to be transported in a series of active and/or passive processes until they reach the site of calcification which is usually located in specialized cellular compartments, tissues, or tissue interfaces. Transport mechanisms and pathways are highly diverse among the various calcifying taxa which rules out the possibility to formulate a generally applicable calcification model (Mann, 2001). What all calcifiers have in common, however, is their dependency on calcium and inorganic carbon availability in seawater as this is the ultimate source medium (Weiner and Addadi, 2011). Thus, biotic calcification will respond to changes in seawater calcium and inorganic carbon when concentrations cross species-specific thresholds.

Calcium is present in seawater in high concentrations ($\sim 10 \text{ mmol kg}^{-1}$) as Ca^{2+} (Zeebe and Wolf-Gladrow, 2001). As this ion is also the form used in the final precipitation reaction (Eq. 1), calcium does not need to be chemically transformed while being transported from seawater to the site of calcification (Allemand et al., 2004; Bentov et al., 2009; Mackinder et al., 2011). This is in clear contrast to CO_3^{2-} where, the relation between ion source from seawater and ion sink during crystallization is considerably more complex since CO_3^{2-} is in constant exchange with HCO_3^- and CO_2 . Thus, CO_3^{2-} used for CaCO_3 crystallization (Eq. 1) at the site of calcification does not have to be taken from the seawater CO_3^{2-} pool but could equally well originate from the CO_2 or HCO_3^- reservoir and be transformed to CO_3^{2-} shortly before reacting with Ca^{2+} .

Despite the unknown seawater DIC source for CaCO_3 precipitation, $[\text{CO}_3^{2-}]$ or the CO_3^{2-} -dependent Ω_{CaCO_3} are often considered a priori as the key carbonate system parameters determining calcification rates or the success of calcifying organisms in the oceans (Kleypas et al., 1999; Beaufort et al., 2011). This assumption is reason-

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able under corrosive conditions (i.e. $\Omega_{\text{CaCO}_3} < 1$) where $[\text{CO}_3^{2-}]$ controls the dissolution of CaCO_3 (Eq. 3). The relevance of $[\text{CO}_3^{2-}]$ for the formation of CaCO_3 is, however, poorly constrained because very little is known about a molecular uptake and transport system that can take CO_3^{2-} from seawater and transfer it to the site of calcification.

This uncertainty leads to the key questions: which inorganic carbon species in seawater is/are utilized and which other carbonate system parameter(s) could be relevant for calcification?

Several physiological studies with different calcifying taxa have addressed these questions by setting up experiments where the influence of individual carbonate system parameters could be studied in isolation. Some of these studies found the best correlations of calcification rates with $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} (e.g. Schneider and Erez, 2006; Gazeau et al., 2011; de Putron et al., 2011; Keul et al., 2013; Waldbusser et al., 2014) while others highlighted the importance of $[\text{HCO}_3^-]$ (e.g. Buitenhuis et al., 1999; Jury et al., 2010). Still others found that the response is not controlled by a single carbonate system parameter but the interplay of two or more. In coccolithophores, for example, calcification rates were repeatedly shown to increase from low to intermediate DIC but decrease again above certain thresholds (Langer et al., 2006; Bach et al., 2011; Sett et al., 2014). This optimum-curve response pattern was explained by the interaction between HCO_3^- and protons (H^+) where HCO_3^- stimulates calcification as substrate and H^+ functions as inhibitor (Bach et al., 2011, 2013, 2015). Similar conclusions have also been made in studies with bivalves (Thomsen et al., 2015) or corals (Jury et al., 2010) where it has been noted that the calcification response to changing carbonate chemistry could be the result of the opposing effects of $[\text{HCO}_3^-]$ and $[\text{H}^+]$.

Jokiel (2011a, b, 2013) went one step further. Based on the results of his work on coral reef calcification he argued that single carbonate chemistry parameters such as $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} have no basic physiological meaning for calcification. Instead, calcification is controlled by the interaction of a “reactant” (i.e. DIC) and an “inhibitor” (i.e. H^+) and that calcification rates only correlate with $[\text{CO}_3^{2-}]$ because $[\text{CO}_3^{2-}]$ itself is lin-

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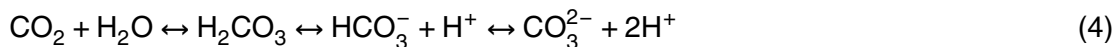
early correlated with the ratio of reactant to inhibitor (i.e. DIC/[H⁺]) (Jokiel, 2013; Jokiel et al., 2014).

The present study builds up on these previous findings and aims to refine the thought that calcification is not controlled by a single carbonate chemistry parameter but reacts to a combination of two or more. Therefore, attention will be drawn to a potentially important proportionality between [CO₃²⁻], or Ω_{CaCO₃}, and the [HCO₃⁻]/[H⁺] ratio which was uncovered by rearranging carbonate chemistry equations. I will discuss (1) how this proportionality could help to understand carbonate chemistry induced changes in CaCO₃ precipitation by marine organisms; (2) how this proportionality could modify the paradigm that high latitude calcifiers are more susceptible to ocean acidification than species living in low latitudes.

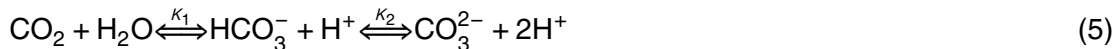
2 Material and methods

2.1 Uncovering the proportionality between [CO₃²⁻], or Ω_{CaCO₃}, and the [HCO₃⁻]/[H⁺] ratio

The carbonate system is an equilibrium reaction of the form:



which can be simplified to:



because [H₂CO₃] is only about 1/1000 of [CO₂] and has no special significance to the acid–base equilibria since both species are uncharged (Butler, 1998; Dickson, 2010). Hence, [CO₂] is summarized in the following as:

$$[\text{CO}_2] = [\text{CO}_2]_{\text{aq}} + [\text{H}_2\text{CO}_3] \quad (6)$$

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where aq denotes for gaseous CO₂ dissolved in seawater.

For the description of the carbonate system, the first and second dissociation constants (K_1 and K_2) are expressed in terms of concentrations – i.e. as stoichiometric dissociation constants:

$$K_1^* = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \quad (7)$$

and

$$K_2^* = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad (8)$$

which are a function of temperature (T), salinity (S), and pressure (P) (Zeebe and Wolf-Gladrow, 2001). Solving Eq. (8) for $[\text{HCO}_3^-]/[\text{H}^+]$ as:

$$\frac{[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{1}{K_2^*} [\text{CO}_3^{2-}] \quad (9)$$

shows that $[\text{CO}_3^{2-}]$ is proportional to $[\text{HCO}_3^-]/[\text{H}^+]$ when temperature, salinity, and pressure remain unchanged because K_2^* is constant under these circumstances.

The CaCO₃ saturation state of seawater has been defined in Eq. (3). Solving Eqs. (3) and (9) for $[\text{CO}_3^{2-}]$ yields:

$$[\text{CO}_3^{2-}] = \frac{\Omega_{\text{CaCO}_3} K_{\text{sp}}^*}{[\text{Ca}^{2+}]} \quad (10)$$

and

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-] K_2^*}{[\text{H}^+]} \quad (11)$$

Combining these equations and subsequently solving them for $[\text{HCO}_3^-]/[\text{H}^+]$ yields:

$$\frac{[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{\Omega_{\text{CaCO}_3} K_{\text{sp}}^*}{[\text{Ca}^{2+}] K_2^*} \quad (12)$$

It follows that $[\text{HCO}_3^-]/[\text{H}^+]$ and Ω_{CaCO_3} are proportional, under constant T , S , and P . Note that $[\text{Ca}^{2+}]$ is conservative in seawater and therefore scales with salinity.

5 2.2 Carbonate chemistry calculations

Carbonate chemistry data presented in Figs. 1–7 were calculated with the MATLAB (the Mathworks) version of CO2SYS (van Heuven et al., 2011) using K_1^* and K_2^* determined by (Millero, 2010), K_{HSO_4} by Dickson (1990), and K_{sp}^* determined by Mucci (1983). $[\text{H}^+]$ (free scale) was subsequently calculated from pH_{free} :

$$10 \text{ pH}_{\text{free}} = -\log[\text{H}^+]_{\text{free}} \quad (13)$$

as given in Zeebe and Wolf-Gladrow (2001).

Surface ocean (0–50 m) carbonate chemistry (DIC, TA), nutrient (PO_4^{3-}), salinity, and temperature data used for calculations presented in Figs. 1 and 5b, d, f, and 6 were extracted from a model simulation with the University of Victoria (UVic) Earth System model performed by Taucher and Oschlies (2011). In their study, the model was spun up for 4000 years with pre-industrial boundary conditions and then forced with reconstructed CO_2 emissions and aerosol dynamics for the period from 1765–2000 (Schmittner et al., 2008). Thereafter, the model was forced with anthropogenic CO_2 emissions as predicted in the IPCC A2 (“business-as-usual”) scenario. Note that the data was taken from their reference run (“TEMP”). For further details on the model setup, please refer to the original description by Taucher and Oschlies (2011).

The ratios $[\text{CO}_3^{2-}]/([\text{HCO}_3^-]/[\text{H}^+])$ and $[\text{CO}_3^{2-}]/(\text{DIC}/[\text{H}^+])$ shown in Fig. 3 were calculated with CO2SYS assuming increasing pCO_2 at constant total alkalinity

(2350 $\mu\text{mol kg}^{-1}$), phosphate and silicate concentrations to be zero, and temperature, salinity, and pressure of 15 °C, 35, and 0 dbar, respectively.

Sensitivities of $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ to changing P , S , or T (Fig. 4) were calculated with CO2SYS assuming phosphate and silicate concentrations to be zero, a constant $p\text{CO}_2$ of 400 μatm , and a constant TA of $\sim 2350 \mu\text{mol kg}^{-1}$. The parameters that were not varied within the particular calculation were set to constant values of 15 °C, 35, and 0 dbar for T , S , and P , respectively.

Calcification related measurements and corresponding DIC, TA, T , S , and nutrient data of experiments with different species (Schneider and Erez, 2006; Gazeau et al., 2011; Keul et al., 2013, Fig. 2) were downloaded from the PANGAEA data server (www.pangaea.de).

Surface ocean (0–100 m) carbonate chemistry, physical, and nutrient data of the meridional Atlantic transect measured during CLIVAR cruises in 2003 (Peltola et al., 2003) and 2005 (Wanninkhof et al., 2006) (Fig. 5a, c, e) were downloaded from the CARINA data synthesis homepage (<http://cdiac.ornl.gov/oceans/CARINA/>). Water column carbonate chemistry, physical, and nutrient data between 1988 and 2012 from the ALOHA time-series station (Fig. 7) in the central Pacific (22°45' N 158°00' W) were downloaded from the ALOHA website (<http://aco-ssds.soest.hawaii.edu/ALOHA/>).

3 Results and discussion

3.1 Is HCO_3^- or CO_3^{2-} the more suitable inorganic carbon substrate for calcification?

It is important to determine the calcification-relevant inorganic carbon species taken from seawater in order to understand the calcification response of marine organisms to changing carbonate chemistry. Most studies assume that HCO_3^- rather than CO_3^{2-} is the key inorganic carbon ion (e.g. Allemand et al., 2004; Mackinder et al., 2010; Stumpp et al., 2012; Taylor et al., 2012). However, proof of this assumption on a physi-

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equilibrium for short periods. In these cases, the utilization of CO_3^{2-} as inorganic carbon source would constitute a substantial risk for the organisms' pH homeostasis. Excess CO_3^{2-} uptake would elevate cytosolic pH while excess CaCO_3 precipitation would reduce it. In contrast, a selective uptake of HCO_3^- from seawater would perturb the cytosolic pH to a much smaller extent when HCO_3^- uptake and CaCO_3 precipitation are not entirely balanced because HCO_3^- has a relatively low potential to accept or donate H^+ at pH 7.2. It may therefore be easier for calcifiers to keep cytosolic pH stable at 7.2 when using HCO_3^- .

- (3) *Stability.* Seawater carbonate chemistry conditions are relatively stable on longer timescales but can fluctuate substantially on a seasonal and diurnal cycle (Takahashi et al., 1993; Thomsen et al., 2010; Shaw et al., 2013), especially in diffusive boundary layers of organisms (Wolf-Gladrow and Riebesell, 1997; Flynn et al., 2012; Glas et al., 2012; Agostini et al., 2013). Fluctuations are mostly induced by photosynthetic or respiratory turnover of CO_2 . The magnitude of fluctuation scales with the productivity of the ecosystem (Schulz and Riebesell, 2013) but fluctuations should usually stay within the ~ 6.5 – 9 pH range. HCO_3^- is dominant and has a relatively stable concentration in this entire pH range, while $[\text{CO}_3^{2-}]$ is highly variable. In the habitat of a temperate coralline algae, for example, typical diurnal pH fluctuations can range from ~ 8.4 at day to ~ 7.6 at night (Cornwall et al., 2013). These changes would translate in a moderate day/night difference of $\sim 30\%$ in $[\text{HCO}_3^-]$ but a pronounced difference of more than 450% in $[\text{CO}_3^{2-}]$. Hence, HCO_3^- is the much more reliable inorganic carbon source for calcification as it shows significantly smaller variability.

3.2 Relationship between calcification and $[\text{CO}_3^{2-}]$ or $[\text{HCO}_3^-]/[\text{H}^+]$ in existing datasets

If the common assumption holds and marine calcifiers primarily utilize HCO_3^- instead of CO_3^{2-} as CaCO_3 substrate (see previous section) then correlations between calcification and $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} are meaningless under non-corrosive conditions. Still, these correlations often yield high coefficients of determination (R^2) even if conditions are super-saturated (Schneider and Erez, 2006; Marubini et al., 2008; de Putron et al., 2011; Gazeau et al., 2011; Keul et al., 2013; Waldbusser et al., 2014). This dilemma can be resolved when considering the proportionality between $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ derived above. Every correlation between calcification and $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} will be identical to the corresponding correlation with $[\text{HCO}_3^-]/[\text{H}^+]$ when T , S , and P are stable (see Eqs. 9, 12).

This is illustrated with data from three publications where the influence different carbonate chemistry parameters on calcification rates was disentangled (Schneider and Erez, 2006; Gazeau et al., 2011; Keul et al., 2013) (Fig. 2). All three studies conclude that $[\text{CO}_3^{2-}]$ determines calcification rates although calcification rates or calcification related measurements of the hermatypic coral *Acropora eurystoma* (Schneider and Erez, 2006), the benthic foraminifer *Ammonia* spec. (Keul et al., 2013), and larvae of the Pacific oyster *Crassostrea gigas* (Gazeau et al., 2011) correlate equally well to $[\text{HCO}_3^-]/[\text{H}^+]$.

3.3 Conceptual basis for the calcification control of $[\text{HCO}_3^-]/[\text{H}^+]$

Implicit in the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio is the thought that biotic CaCO_3 precipitation is balanced by the stimulating influence of an inorganic carbon substrate and the negative influence of an inhibitor (Bach et al., 2011, 2013, 2015; Jokiel, 2011a, b, 2013; Jokiel

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et al., 2014). Higher $[\text{HCO}_3^-]$ would stimulate calcification rates as a substrate whereas high seawater $[\text{H}^+]$ would inhibit them.

When both, $[\text{HCO}_3^-]$ and $[\text{H}^+]$ increase, calcification would be balanced by the degree of change of these two ions. $[\text{H}^+]$ increases profoundly under ocean acidification while $[\text{HCO}_3^-]$ increases only marginally (Fig. 1, see also Schulz et al., 2009). Here, changing $[\text{H}^+]$ should be of dominant control (Bach et al., 2011). When increasing $[\text{H}^+]$ is paralleled by a significant increase of $[\text{HCO}_3^-]$, then the additional bicarbonate could potentially compensate the inhibitory proton effect to some extent (Bach et al., 2015). Indeed, HCO_3^- uptake is a common mechanism to buffer acidosis and might be facilitated at higher HCO_3^- availability (Boron, 2004; Melzner et al., 2009; Stumpp et al., 2012).

The inhibition by high seawater $[\text{H}^+]$ is tightly linked to the production of CaCO_3 from Ca^{2+} and HCO_3^- because calcification is then a source of H^+ ($\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}^+$). H^+ generated that way would subsequently have to be released back into seawater to avoid acidification at the site of calcification. This removal should be relatively easy when seawater $[\text{H}^+]$ is low (i.e. pH is high). It could become more difficult, however, when seawater $[\text{H}^+]$ rises and the inside-out $[\text{H}^+]$ gradient shrinks (Jokiel, 2011b; Taylor et al., 2011; Stumpp et al., 2012; Venn et al., 2013).

3.4 Similarities and differences between the $\text{DIC}/[\text{H}^+]$ and the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio

In a series of papers Jokiel (2011a, 2011b, 2013) proposed that carbonate chemistry controls calcification rates in corals through the combined influence of DIC (“reactant”) and H^+ (“inhibitor”) and noted that favorable carbonate chemistry conditions are established when the ratio of DIC to $[\text{H}^+]$ is high. Hence, the underlying thought implicit in the $\text{DIC}/[\text{H}^+]$ ratio is identical to that implemented in the “substrate-inhibitor-ratio” defined here as $[\text{HCO}_3^-]/[\text{H}^+]$.

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Jokiel (2011a, b, 2013) also noted that there is a linear correlation between $\text{DIC}/[\text{H}^+]$ and $[\text{CO}_3^{2-}]$. The correlation observed by Jokiel exists because the DIC pool is dominated by HCO_3^- ions under normal pH conditions (see Sect. 3.1) and therefore typically follows the same rules as the proportionality between $[\text{HCO}_3^-]/[\text{H}^+]$ and $[\text{CO}_3^{2-}]$ uncovered in Sect. 2.1. However, when the fraction of HCO_3^- in the DIC pool declines, the $\text{DIC}/[\text{H}^+]$ vs. $[\text{CO}_3^{2-}]$ correlation starts to increasingly deviate from linearity. In the oceans, noticeable deviations start in the $p\text{CO}_2$ range below 250–500 μatm , where an exponentially increasing fraction of the DIC pool is present as CO_3^{2-} (Fig. 3). Thus, exchanging $\text{DIC}/[\text{H}^+]$ with $[\text{CO}_3^{2-}]$ to explain the calcification response to carbonate chemistry (comparable to what has been done in Fig. 2) is not meaningful when $p\text{CO}_2$ is below this range. This problem does not exist for the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio where the linear relation holds under all carbonate chemistry conditions as long as T , S , and P are constant (Fig. 3).

Whether the $\text{DIC}/[\text{H}^+]$ ratio proposed by Jokiel (2011a, b, 2013) or the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio could be the more meaningful parameter to explain the carbonate chemistry response of calcification depends on the investigated organism. The $\text{DIC}/[\text{H}^+]$ ratio would be more meaningful if the organism takes up all DIC species in the same proportion as present in seawater while the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio would be more appropriate when selective uptake on HCO_3^- occurs (see also Sect. 3.6.3).

3.5 Global implications

The proportionality between $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ derived in Sect. 2.1 is only valid as long temperature, salinity, and pressure are constant and do not alter K_2^* and K_{sp}^* . If these parameters change, then the proportionality no longer holds and the response of calcification would be different, depending on whether calcifiers react to $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , or $[\text{HCO}_3^-]/[\text{H}^+]$.

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The influence of temperature, salinity, and pressure is illustrated in Fig. 4. Increasing pressure has a negative effect on all three carbonate system components. It is most pronounced on Ω_{CaCO_3} and weakest on $[\text{CO}_3^{2-}]$ (Fig. 4a). Increasing salinity has a positive influence on $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} but a negative one on $[\text{HCO}_3^-]/[\text{H}^+]$ (Fig. 4b). Its influence, however, is low since salinity gradients in the oceans are generally too weak to be of high relevance in this context. Increasing temperature has a profound positive impact on $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} but almost no influence on $[\text{HCO}_3^-]/[\text{H}^+]$ (Fig. 4c).

In combination, these factors cause a highly interesting difference of $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ on a latitudinal gradient. While Ω_{CaCO_3} and $[\text{CO}_3^{2-}]$ decrease 2–3 fold towards the poles, $[\text{HCO}_3^-]/[\text{H}^+]$ is almost constant over the same range (Figs. 5 and 6). This inconsistency is mostly due to different temperature sensitivities among the three parameters. Cooler temperatures in high latitudes lead to higher solubility of CO_2 which results in an equilibrium shift away from $[\text{CO}_3^{2-}]$ towards $[\text{CO}_2]$ and $[\text{HCO}_3^-]$ (Eq. 4). Accordingly, $[\text{CO}_3^{2-}]$ declines towards the poles. Ω_{CaCO_3} follows the concentration of CO_3^{2-} since $[\text{Ca}^{2+}]$ is too stable to be of any relevance. The slight poleward increase of $[\text{HCO}_3^-]$ is balanced by the concomitant increase in $[\text{H}^+]$ which explains the stability of $[\text{HCO}_3^-]/[\text{H}^+]$ over the latitudinal gradient. Thus, carbonate chemistry conditions for biotic CaCO_3 production would be fairly constant over the entire surface ocean if controlled by $[\text{HCO}_3^-]/[\text{H}^+]$, whereas they would show a profound poleward deterioration if determined by $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} (Figs. 5 and 6).

Vertically, $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} decrease more severely than $[\text{HCO}_3^-]/[\text{H}^+]$ from surface to about a thousand meters depth (~ 5 fold vs. ~ 3 fold decrease, Fig. 7). This has two reasons. First, the temperature decline, which is strongest in the upper few hundred meters, negatively affects $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} whereas $[\text{HCO}_3^-]/[\text{H}^+]$ remains unaffected (Fig. 4c). Second, the increase of $[\text{H}^+]$ from 0–1000 m due to respiratory CO_2 release is paralleled by $\sim 30\%$ increases of $[\text{HCO}_3^-]$ which mitigates the decline of $[\text{HCO}_3^-]/[\text{H}^+]$. Below a thousand meters, all three carbonate system param-

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eters are relatively stable. Of the three carbonate system parameters considered here, $[\text{HCO}_3^-]/[\text{H}^+]$ is the most homogeneous when comparing the development over the entire water column. Thus, the deterioration of carbonate chemistry conditions for biotic CaCO_3 production with depth would be less pronounced if it was controlled by $[\text{HCO}_3^-]/[\text{H}^+]$ (Fig. 7).

The ongoing perturbation of the surface ocean by anthropogenic CO_2 causes a decline of Ω_{CaCO_3} , $[\text{CO}_3^{2-}]$, and $[\text{HCO}_3^-]/[\text{H}^+]$. The magnitude of change in all three parameters is very similar to each other on global average (Fig. 1). Until 2100 they decrease to about half the value in the year 2000 (Figs. 1, 5). The two different latitudinal patterns for Ω_{CaCO_3} , $[\text{CO}_3^{2-}]$, or $[\text{HCO}_3^-]/[\text{H}^+]$ are, however, conserved in the course of climate change (Fig. 6). Hence, latitudinal differences among the three parameters are prevailing for longer timescales and are not restricted to the current status of the carbonate system.

The presence of two highly different latitudinal patterns has important implications for ocean acidification research. Polar regions have been identified as the most severely acidification-affected regions on Earth as they are the first to experience corrosive conditions (i.e. $\Omega_{\text{CaCO}_3} < 1$; Orr et al., 2005; Fabry et al., 2009; Hofmann et al., 2010). The vulnerability of high latitudes is therefore explained by an abiotic process – i.e. CaCO_3 dissolution. The study presented here deals with controls on the opposite process – i.e. biotic CaCO_3 formation. Dissolution is determined by Ω_{CaCO_3} and there is no doubt that polar regions are most severely affected (see also Fig. 6). From the production perspective, however, this is not necessarily the case. Ocean acidification would be equally harmful in warm-water habitats as in the polar realm in case CaCO_3 formation is controlled by $[\text{HCO}_3^-]/[\text{H}^+]$ and not $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} . Thus, when high latitude organisms find a way to efficiently protect their crystal skeletons from corrosive seawater, then they may not be more vulnerable to ocean acidification than their warm water counterparts.

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3.6 Limitations and uncertainties

This study has argued that a substrate-inhibitor ratio like $[\text{HCO}_3^-]/[\text{H}^+]$ (or $\text{DIC}/[\text{H}^+]$; Jokiel, 2011a, 2011b, 2013) could be a useful measure to assess which carbonate chemistry conditions could be favorable for calcification. However, it must also be recognized that such a rather general view on carbonate chemistry control of calcification has its limitations when it comes to a more detailed physiological level. Calcification follows an enormous variety of pathways among the different taxa, with distinct inorganic carbon uptake mechanisms, and distinct sensitivities to H^+ . Thus, the capability of the substrate-inhibitor ratio to predict calcification rates can always be confounded by taxon-specific physiological features. The most important limitations and uncertainties for the ability of $[\text{HCO}_3^-]/[\text{H}^+]$ to serve as predictor variable for the carbonate chemistry control of calcification will be discussed in the following.

3.6.1 Corrosive conditions

When discussing the influence of carbonate chemistry on calcification, distinction needs to be made between production and dissolution of CaCO_3 since these two processes are possibly controlled by different carbonate chemistry parameters. The ratio of $[\text{HCO}_3^-]$ and $[\text{H}^+]$ can potentially be very useful to determine the production of CaCO_3 but its influence would be obscured by the abiotic influence of $[\text{CO}_3^{2-}]$ on the dissolution of CaCO_3 when Ω_{CaCO_3} is below one. Accordingly, corrosive conditions would require consideration of both $[\text{HCO}_3^-]/[\text{H}^+]$ and Ω_{CaCO_3} in order to correctly estimate the impact of carbonate chemistry on biotic CaCO_3 formation. Areas with corrosive conditions will expand under ocean acidification (Orr et al., 2005) so that CaCO_3 dissolution becomes more widespread problem for future calcifiers. However, dealing with dissolution of CaCO_3 is only of secondary relevance for living organisms as everything that dissolves needs to be formed in the first place. Hence, although dissolution processes cannot be left unconsidered, it is reasonable from a biological point of view to focus on the processes that control formation of CaCO_3 .

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3.6.2 Extreme concentrations of HCO_3^- and H^+

In some studies, calcification rates correlated better with $[\text{HCO}_3^-]$ than with $[\text{CO}_3^{2-}]$ (and thus $[\text{HCO}_3^-]/[\text{H}^+]$) (Bach et al., 2013; Jury et al., 2010), which challenges the potential of $[\text{HCO}_3^-]/[\text{H}^+]$ to serve as predictor variable for CaCO_3 production. However, the dominant control of HCO_3^- in these particular studies can be easily understood when considering the low HCO_3^- concentrations at which its dominance actually occurred. The influence of $[\text{HCO}_3^-]$ relative to $[\text{H}^+]$ will become more and more influential under conditions where HCO_3^- becomes increasingly limiting. Conversely, any influence of $[\text{HCO}_3^-]$ will become negligible when the organism is fully saturated with it. Under these circumstances calcification is most likely primarily controlled by $[\text{H}^+]$ (Bach et al., 2011; Jokiel, 2011b; Taylor et al., 2011). Thus, the potential of $[\text{HCO}_3^-]/[\text{H}^+]$ in predicting calcification is low at rather “extreme” carbonate chemistry conditions where the influence of either HCO_3^- or H^+ strongly outweighs the other. Its potential should be high, however, under conditions where the investigated organism is responsive to both $[\text{HCO}_3^-]$ and $[\text{H}^+]$.

3.6.3 Transport of seawater

Some foraminifera and coral species have been reported to transfer calcification-relevant ions to the site of CaCO_3 precipitation by means of seawater transport (Bentov et al., 2009; de Nooijer et al., 2009; Gagnon et al., 2012; Tambutté et al., 2012). In the case of foraminifera, seawater is engulfed in membrane vesicles, transported to the site of calcification, and on its way alkalized to increase $[\text{CO}_3^{2-}]$ (Bentov et al., 2009; de Nooijer et al., 2009). In the case of corals, seawater (or at least its constituents smaller 20 nm; Tambutté et al., 2012) may pass epithelia and reach the CaCO_3 skeleton via the paracellular pathway. For both processes (seawater endocytosis and seawater leakage along the intercellular space), all DIC species are potential inorganic carbon sources to fuel calcification. Hence, for organisms which purely rely on seawater

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ter endocytosis/leakage, the DIC : [H+] ratio proposed by Jokiel (2011a, b, 2013) could be more appropriate to explain the calcification response to carbonate chemistry than [HCO₃⁻]/[H⁺].

3.6.4 Inorganic carbon from respiratory sources

Some organisms receive significant amounts of inorganic carbon used for calcification from respiratory sources (Pearse, 1970; Erez, 1978; Sikes et al., 1981; Tanaka et al., 1986; Furla et al., 2000). Here, organisms do not exclusively rely on direct inorganic carbon utilization from seawater but supplement calcification to a variable degree with CO₂ gained intracellularly from respired biomass. Thus, the potential control of seawater [HCO₃⁻]/[H⁺] on calcification in these particular organisms may be weakened by the degree to which they utilize CO₂ from respiration.

3.6.5 Photoautotrophic calcifiers

Photoautotrophic calcifiers such as coccolithophores or zooxanthellate corals not only interact with HCO₃⁻ and H⁺ but also with CO₂. Photosynthetic and calcification-related processes are physiologically coupled within photoautotrophs (Paasche, 2002; Allemand et al., 2004;). Accordingly, calcification rates will be affected indirectly when photosynthesis is CO₂ limited (Bach et al., 2015). A valuable measure to determine the potential of CO₂ to limit growth and photosynthesis is $K_{1/2}$ which denotes the CO₂ concentration where the process runs at half of its maximum. Available $K_{1/2}$ measurements suggest that CO₂ limitation mostly occurs well below CO₂ concentrations typically encountered by the organisms in their respective habitats (Rost et al., 2003; Sett et al., 2014). Thus, its influence should rarely interfere with the influence of [HCO₃⁻]/[H⁺] under natural conditions.

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A variety of studies highlighted that carbonate chemistry controls calcification through the balance of stimulation by an inorganic carbon substrate (HCO_3^- or DIC) and inhibition by protons (e.g. Bach et al., 2011, 2015; Jokiel, 2011a; Thomsen et al., 2015).

5 Other studies found that $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} are the carbonate chemistry parameters which best predict calcification (e.g. Schneider and Erez, 2006; de Putron et al., 2011; Gazeau et al., 2011; Waldbusser et al., 2014). The proportionalities between $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} and the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio derived in Eqs. (9) and (12) provide the chemical basis to reconcile these conflicting results. Every correlation between calcification and
10 $[\text{CO}_3^{2-}]$ or Ω_{CaCO_3} will be identical to the corresponding correlation with $[\text{HCO}_3^-]/[\text{H}^+]$ when T , S , and P are stable. Thus, the good correlations to $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} that have previously been reported may have simply masked the combined influence of $[\text{HCO}_3^-]$ and $[\text{H}^+]$ (see also findings by Jokiel 2011a, b, 2013; Jokiel et al., 2014) which are arguably the physiologically more meaningful parameters to correlate calcification with (Bach et al., 2013; Jokiel, 2013; Thomsen et al., 2015; Sects. 3.1 and 3.3).
15

Accounting for the influence of $[\text{HCO}_3^-]/[\text{H}^+]$ in controlling CaCO_3 formation would also have interesting implications for how we assess carbonate chemistry conditions and calcification along a latitudinal gradient. A comparison of present and future $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ patterns in the surface ocean revealed a strong
20 poleward decline in $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} but no decline in $[\text{HCO}_3^-]/[\text{H}^+]$. These highly different latitudinal patterns are conserved during climate change. Thus, it may turn out that ocean acidification is globally a more uniform problem for biotic CaCO_3 formation than previously thought.

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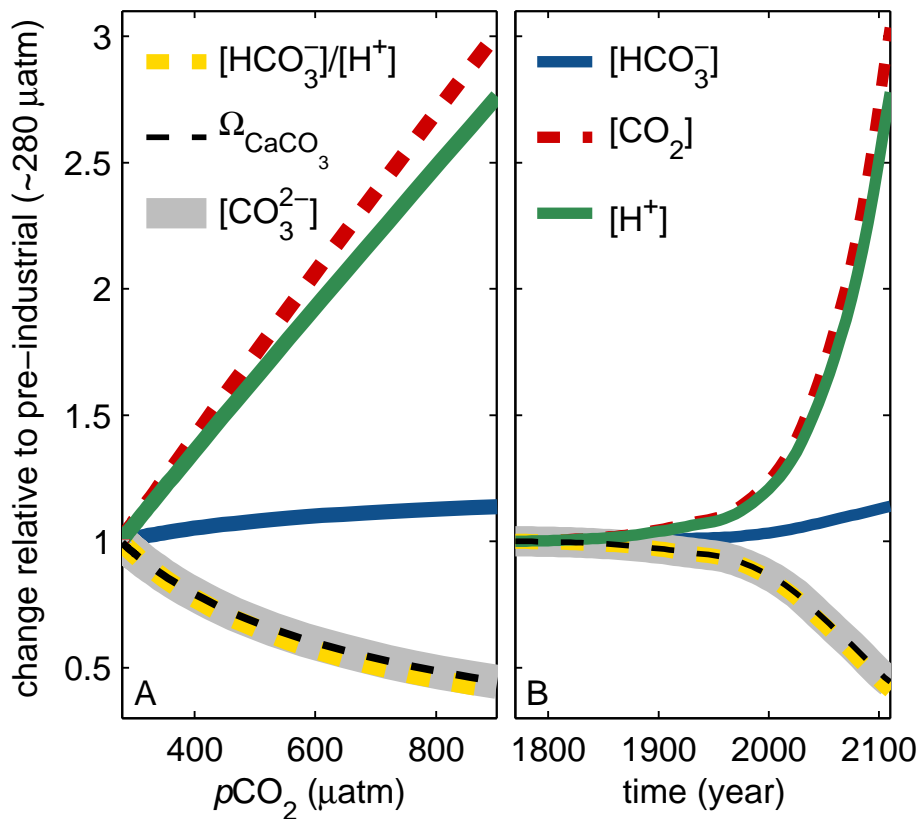


Figure 1. Change of different surface ocean carbonate chemistry parameters under “business-as-usual” climate change scenario SRES A2 with (a) increasing atmospheric $p\text{CO}_2$ and (b) over time. All changes are relative to the pre-industrial CO_2 partial pressure of $\sim 280 \mu\text{atm}$. Note that the slight deviations from proportionality between $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ are the result of changes in global average temperature and salinity in the course of climate change which affect K_2^* and K_{sp}^* (see Sect. 3.5 for further details).

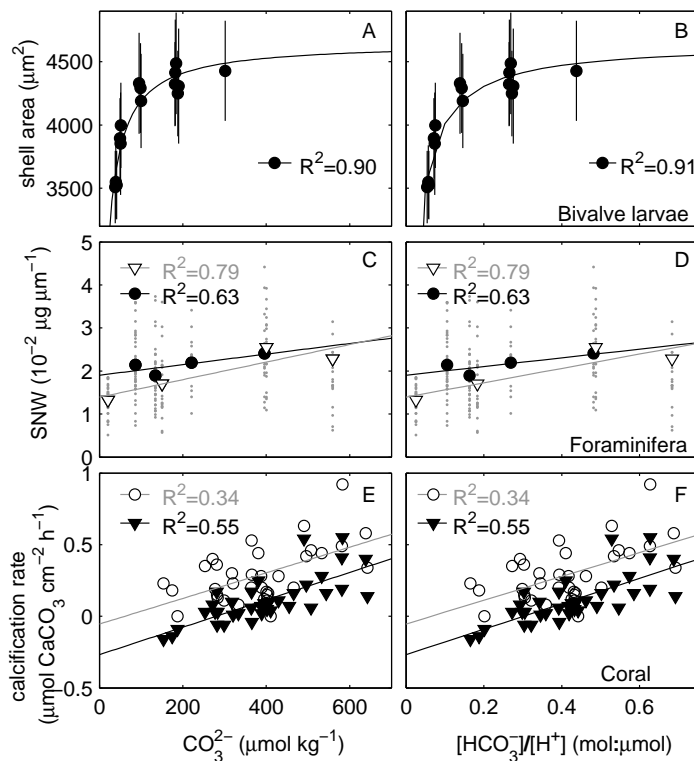


Figure 2. Correlations between calcification related measurements and $[\text{CO}_3^{2-}]$ (left panel) or $[\text{HCO}_3^-]/[\text{H}^+]$ (right panel). **(a, b)** Shell areas of D-veliger larvae reached 3 days after incubating embryos of the Pacific oyster *Crassostrea gigas* (Gazeau et al., 2011). **(c, d)** Size normalized weight (SNW) of the foraminifer *Ammonia spec.* in its asexually reproducing life cycle stage (Keul et al., 2013). Black dots: constant DIC, variable CO_2 . White triangles: constant pH, variable CO_2 . **(e, f)** Calcification rates of the symbiont-bearing hermatypic coral *Acropora eurysoma* (Schneider and Erez, 2006). White dots and black triangles refer to incubations at light and dark, respectively.

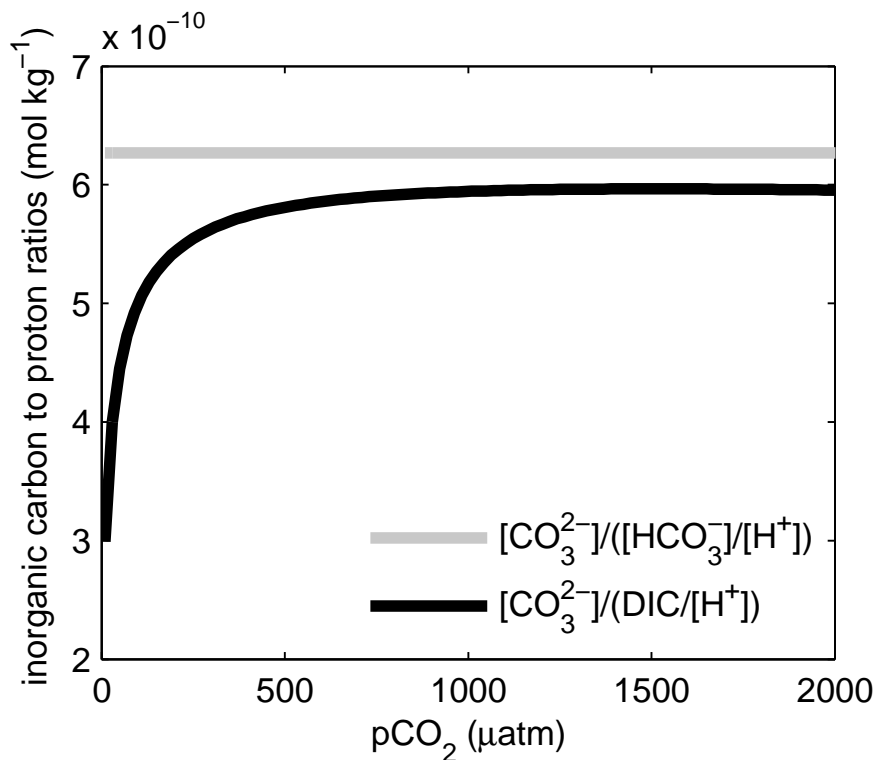


Figure 3. Ratio of $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]/[\text{H}^+]$ compared to the ratio of $[\text{CO}_3^{2-}]$ and $\text{DIC}/[\text{H}^+]$. $[\text{CO}_3^{2-}]/([\text{HCO}_3^-]/[\text{H}^+])$ is constant, since CO_3^{2-} and $[\text{HCO}_3^-]/[\text{H}^+]$ are proportional to each other under constant temperature, salinity and pressure (Eq. 9). In contrast, the correlation between $[\text{CO}_3^{2-}]$ and $\text{DIC}/[\text{H}^+]$ only works well when the majority of DIC is found in the HCO_3^- pool. This is the case for $p\text{CO}_2$ values larger than $\sim 250\text{--}500\ \mu\text{atm}$, where $[\text{CO}_3^{2-}]/(\text{DIC}/[\text{H}^+])$ shows very little change. Below this threshold, however, the correlation starts deviating from linearity since an exponentially increasing proportion of the DIC pool is present as CO_3^{2-} .

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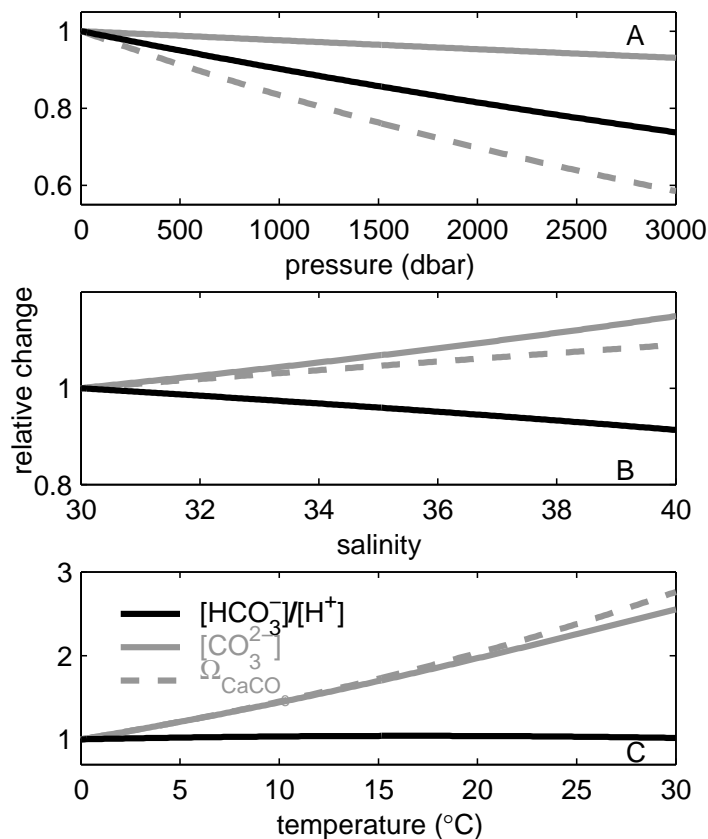


Figure 4. Relative change of $[\text{CO}_3^{2-}]$, Ω_{CaCO_3} , and $[\text{HCO}_3^-]/[\text{H}^+]$ on (a) a pressure gradient, (b) a salinity gradient, and (c) a temperature gradient.

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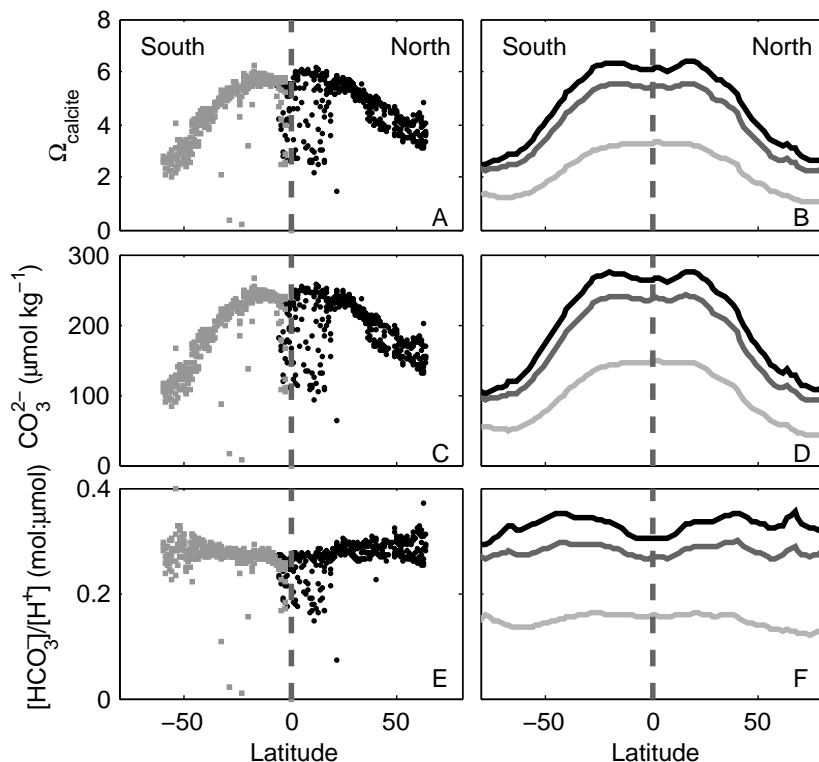


Figure 5. Change of Ω_{CaCO_3} , $[\text{CO}_3^{2-}]$, and $[\text{HCO}_3^-]/[\text{H}^+]$ in the surface ocean along a meridional gradient. The left panel (a, c, and e) shows compiled surface ocean (0–100 m) data from two north to south transects in the Atlantic, measured during CLIVAR CO_2 cruises in 2003 (black dots) and 2005 (grey squares), respectively. The right panel (b, d, and f) shows the latitudinal surface ocean (0–50 m) average calculated with the UVic model for the years 1770 (black line), 2000 (grey line), and 2100 (light grey line). The dotted vertical line illustrates the equator.

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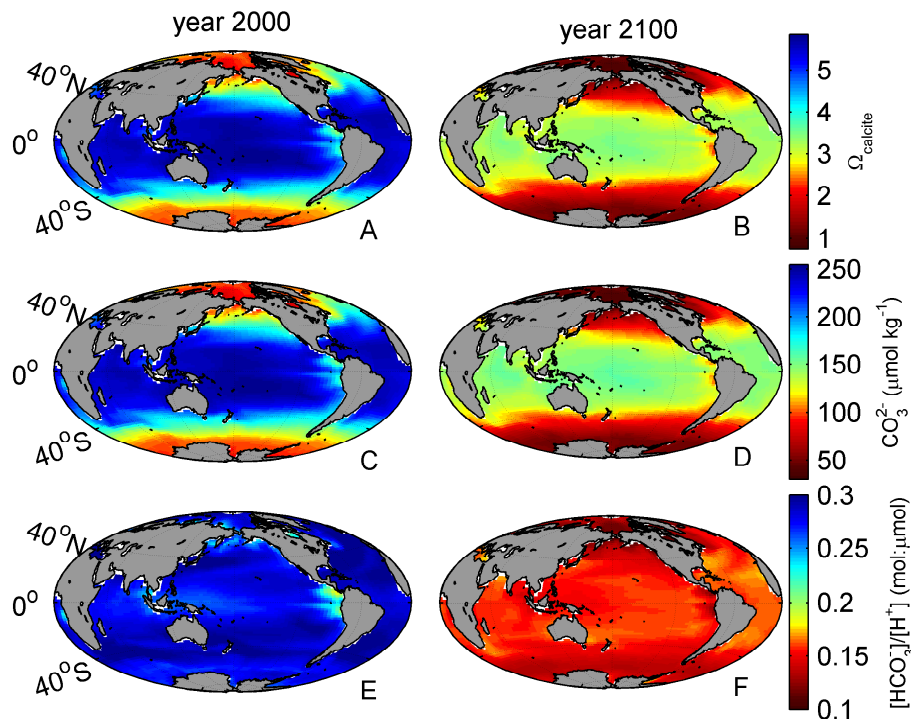


Figure 6. Surface ocean (0–50 m) Ω_{CaCO_3} (a, b), $[\text{CO}_3^{2-}]$ (c, d), and $[\text{HCO}_3^-]/[\text{H}^+]$ (e, f) in the year 2000 (left panel) compared to 2100 (right panel) calculated with the UVic model. The pronounced latitudinal gradient of Ω_{CaCO_3} and $[\text{CO}_3^{2-}]$ is absent in $[\text{HCO}_3^-]/[\text{H}^+]$ (see also Fig. 5). $[\text{HCO}_3^-]/[\text{H}^+]$ is quite homogeneous in 2000 and 2100 in all major ocean basins, with only some regional anomalies. These are found in some coastal areas (e.g. in the Bering Sea) and in eastern boundary upwelling systems, most noticeably off the west coast of South and Central America.

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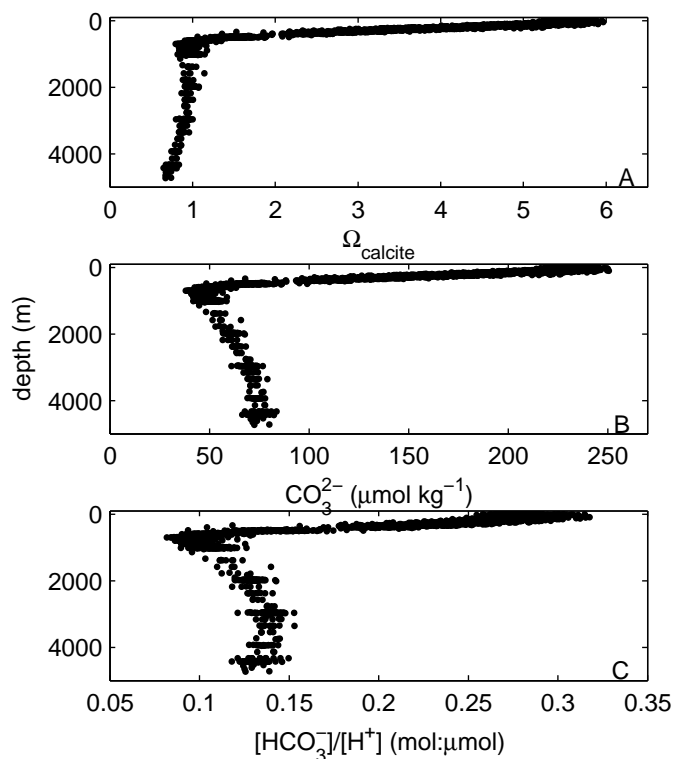


Figure 7. Change of (a) Ω_{calcite} , (b) $[\text{CO}_3^{2-}]$, and (c) $[\text{HCO}_3^-]/[\text{H}^+]$ on a depth gradient at ALOHA time-series station near Hawaii ($22^\circ 45' \text{ N } 158^\circ 00' \text{ W}$). Compiled data from 1988–2012 which was downloaded from the ALOHA website (<http://aco-ssds.soest.hawaii.edu/ALOHA/>).