Ocean Acidification in the Coastal Zone from an Organism's Perspective: Multiple System Parameters, Frequency Domains, and Habitats

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Abstract

Multiple natural and anthropogenic processes alter the carbonate chemistry of the coastal zone in ways that either exacerbate or mitigate ocean acidification effects. Freshwater inputs and multiple acid-base reactions change carbonate chemistry conditions, sometimes synergistically. The shallow nature of these systems results in strong benthic-pelagic coupling, and marine invertebrates at different life history stages rely on both benthic and pelagic habitats. Carbonate chemistry in coastal systems can be highly variable, responding to processes with temporal modes ranging from seconds to centuries. Identifying scales of variability relevant to levels of biological organization requires a fuller characterization of both the frequency and magnitude domains of processes contributing to or reducing acidification in pelagic and benthic habitats. We review the processes that contribute to coastal acidification with attention to timescales of variability and habitats relevant to marine bivalves.

1. INTRODUCTION AND PERSPECTIVE

Anthropogenic CO_2: the CO_2 in the Earth's various systems resulting from human fossil fuel use and cement production

Ocean acidification has become a topic of great public interest and a focus of significant research effort in recent years. The increasing anthropogenic carbon dioxide (CO_2) in seawater and resulting acidification of ocean waters are well documented and follow simple thermodynamic relationships. How ocean acidification will affect ecologically and economically important organisms in coastal habitats is more difficult to robustly predict because carbonate chemistry can be highly variable, conditions that organisms are actually exposed to are difficult to measure, and organism sensitivity can vary across life history stages and in conjunction with other stressors. These challenges to simple predictions of winners and losers in a high-CO_2 world are formidable. This review focuses on the processes that contribute to temporal variability in coastal-zone carbonate chemistry and, ultimately, to the conditions experienced by a model taxon, marine bivalves. We first discuss recent work on climate change and thermal stress to provide context for understanding acidification stress. We then examine processes that alter pelagic and benthic carbonate chemistry, and summarize briefly some of the key habitats where bivalves live and how CO_2 conditions in those habitats may differ from globally averaged CO_2 values.

The carbonate chemistry and thus the pH of marine and estuarine waters are not static; they vary temporally and spatially as a result of many processes, some natural and some from anthropogenic disturbance. The dynamic range of many coastal carbonate system parameters, even over a 24-h period, often exceeds projections of end-of-century change in oceanic carbonate chemistry resulting from increasing atmospheric CO_2. Such dynamic range does not preclude us from trying to understand how the various processes modifying coastal carbonate chemistry interact to affect organisms in these habitats, nor does it mean a priori that organisms in coastal environments are better adapted to higher CO_2 levels (Jansson et al. 2013). As an analogy, organisms adapted to warm environments simply appear to be closer to thermal thresholds than cold-adapted organisms are (Somero 2012), and plasticity in physiology may be costly to other functions, such as reproduction (Hofmann & Todgham 2010). In estuarine zones with highly variable salinity, diversity is lower because fewer organisms can cope with the extremes. Further, as recently noted by Wethey et al. (2011), extreme temperature events are principal drivers of biogeographic redistribution. Are biological responses to a different environmental stressor, ocean acidification, fundamentally different?

We submit that a comprehensive accounting of both mean and extreme carbonate system conditions, as well as their respective time and space scales, is necessary to understand how coastal marine communities will respond to future acidification challenges. Indeed, one can argue that extreme events in carbonate chemistry will impact organisms more directly than the gradual increase in atmospheric CO_2. However, the gradual increase in baseline CO_2 will presumably increase the incidence of extreme events. Hauri et al. (2013a,b) and Harris et al. (2013), for example, showed that a slowly shifting CO_2 baseline in the California Current ecosystem has already increased the frequency, magnitude, and duration of extreme events, and has led to conditions that either exceed important thresholds for organisms or have moved outside the normal range under preindustrial CO_2 levels. Trends of longer-term discrete or mean values do not generally capture the occurrence of extreme events and the range in carbonate system parameters (e.g., Waldbusser et al. 2011b, Duarte et al. 2013); rather, those trends may provide a cursory diagnosis of the general direction of system change. Recent work has highlighted the importance of an organismal perspective in considering the dynamic, habitat-specific carbonate system conditions of the coastal zone as opposed to the globally averaged conditions (Hofmann et al. 2011, Barton et al. 2012, Busch & McElhany 2013, Duarte et al. 2013, Gobler & Talmage 2013). Our motivation in this review is therefore to address the processes that alter carbonate chemistry in the coastal zone from an organismal perspective.

① Increasing pCO_2 increases **carbonic acid** $CO_{2(g)} \rightarrow CO_{2(aq)} + H_2O \rightarrow H_2CO_3$

② Increasing **carbonic acid** results in titration of **carbonate ions** $H_2CO_3 + CO_3^{2-} \rightarrow 2HCO_3^-$

③ pH is driven largely by the ratio of **carbonic acid** to **carbonate ions** (pH = –log[H⁺]) $[H^+] = \sqrt{[K_1 \cdot K_2] \cdot \left[\frac{H_2CO_3}{CO_3^-}\right]}$

④ **Saturation state** is driven by total **carbonate ions** $\Omega_{CaCO_3} = \frac{[Ca^{2+}][CO_3^{2-}]}{K^*_{sp\text{-}CaCO_3}}$

⑤ **Other acid-base** reactions can alter **pH** and thus **carbonate ion** concentration

⑥ **Alkalinity** is generally proportional to **salinity**

Figure 1

Key concepts of carbonate chemistry. ① CO_2 gas dissolves in seawater and forms weak carbonic acid (H_2CO_3). ② The carbonic acid then quickly dissociates at seawater pH and produces protons that titrate CO_3^{2-}. These first two reactions are reversible and rarely complete. ③ Because dissolved CO_2 forms carbonic acid, and most of this carbonic acid then dissociates, an increasing level of aqueous CO_2 results in nondissociated carbonic acid, as the CO_3^{2-} required to titrate the protons is consumed. Dissolved inorganic carbon is abundant in seawater, and its speciation generally controls pH. The K_1 and K_2 terms refer to carbonic acid's first and second dissociation constants (the first for H_2CO_3 into HCO_3^-, and then the second for HCO_3^- into CO_3^{2-}), respectively. ④ The saturation state (Ω) is a measure of the thermodynamic stability of a calcium carbonate mineral ($CaCO_3$) and is a function of the calcium and carbonate ion concentration over the stoichiometric solubility constant ($K^*_{sp\text{-}CaCO_3}$); this constant, in turn, is a function of temperature, salinity, and pressure. ⑤ In coastal waters, other acid-base pairs (e.g., silicate and phosphate) can perturb pH and the speciation of the carbonate system if they are present at a sufficient concentration. ⑥ Total alkalinity is generally proportional to salinity but also varies regionally depending on watershed attributes and local net biological productivity. Additionally, charged organic matter can sometimes contribute significantly to the total alkalinity in mesohaline waters.

1.1. A Carbonate Chemistry Perspective from Coastal Zones

The pH of seawater, presently ~8.1, is largely a function of the dissociation of dissolved inorganic carbon (DIC), whose relative proportions by mass are ~0.5% aqueous CO_2, ~89% bicarbonate (HCO_3^-), and ~11% carbonate ions (CO_3^{2-}). In the ocean, these components sum to ~2,200 μmol kg^{-1}. The delivery of rock-weathering products to the oceans via rivers provides a supply of DIC predominantly as HCO_3^-, with a global average concentration of ~1,100 μmol kg^{-1} (Cai et al. 2008). Rainwater equilibrated with atmospheric CO_2 at 20°C has DIC proportions of approximately 84% CO_2 and 16% HCO_3^-, resulting in a pH of approximately 5.6. **Figure 1** summarizes several key concepts of carbonate chemistry (for additional details, we refer readers to Zeebe & Wolf-Gladrow 2001 and Zeebe 2012).

The global ocean acidification problem is caused by the rate of increase in atmospheric CO_2 exceeding the rate at which weathering, transport, and mixing processes can deliver HCO_3^- and CO_3^{2-} to buffer against the increased carbonic acid (H_2CO_3). This results in decreases in both pH and CO_3^{2-}, which then decreases the thermodynamic stability (saturation state) of calcium carbonate ($CaCO_3$). Hönisch et al. (2012) and Zeebe (2012) articulated such a dynamic, that slower increases in global CO_2 relative to weathering rates would decouple pH and $CaCO_3$ saturation

Dissolved inorganic carbon (DIC): the sum of aqueous dissolved CO_2, carbonic acid, bicarbonate, and carbonate

Saturation state: a measure of the potential in natural waters for a given mineral (e.g., $CaCO_3$) to dissolve, where values less than 1 indicate corrosive conditions; also denoted by Ω

Calcium carbonate ($CaCO_3$): a primary mineral for the formation of shell material, which may be found as aragonite, as calcite, and in other forms state (i.e., the ratio of H_2CO_3 to CO_3^{2-} remains similar, while CO_3^{2-} concentration increases). This geological perspective on ocean acidification can be applied to coastal zones, where carbonate system parameters can decouple owing to multiple processes that may exacerbate changes in global average conditions.

Carbonate weather: local conditions of carbonate chemistry in coastal waters and their variability over timescales of days to months

Carbonate climate: average regional conditions of carbonate chemistry and their variability over timescales of centuries or longer

We may broadly categorize the processes that alter coastal carbonate chemistry as (*a*) chemical reactions that change the abundance and speciation of acid-base compounds, and (*b*) hydrological changes that alter salinity and thus alkalinity. Changes in alkalinity also then affect both the total carbonate ion concentration and the sensitivity to acid-base reactions. The primary biogeochemical processes that alter pH and alkalinity have been thoroughly reviewed elsewhere (e.g., Soetaert et al. 2007). Most germane to the current discussion are processes that alter CO_2 (directly or indirectly), those that change variable ocean-freshwater mixing rates, and those that affect the chemical and physical nature of terrestrial discharge. Because these and other drivers operate across time and space scales (Duarte et al. 2013), knowledge of how processes (and their attendant scales) interact to amplify or dampen carbonate chemistry variability is crucial for understanding coastal acidification.

1.2. Frequency Domain of Chemical Processes in the Coastal Zone

In coastal waters, near-term acidification effects on organisms may be better quantified by the frequency, amplitude, and duration of carbonate chemistry events that cross important organismal thresholds. The combination of acid-base reactions and changes in local hydrology creates localized "carbonate weather" variability that is relevant to the life cycles of marine bivalves. As in the global system, it is important to note that the longer-term carbonate climate will ultimately affect localized coastal carbonate weather conditions, including extreme events. Several recent reviews have provided perspectives on organismal responses to global change (Hofmann & Todgham 2010, Firth & Hawkins 2011, Somero 2012), and we believe that climate and thermal stress and sea-level rise provide analogous frameworks for evaluating the impacts of coastal acidification on organisms. Exemplifying the distinction between climate and weather, Helmuth et al. (2010) documented similarities in year-to-year annual temperatures but significant differences in the occurrence of extreme temperature events harmful to intertidal mussels. An additional analog may be seen in sea-level rise: It is not the gradual increase that affects low-lying property, but rather larger storm surges on top of the slightly higher baseline sea level.

Although others have argued that ocean acidification is primarily an open-ocean problem (Duarte et al. 2013), we suggest that this argument misses the key component of habitat-specific carbonate weather (e.g., Evans et al. 2011, Gruber et al. 2012, Manzello et al. 2012, Hauri et al. 2013b) and the conditions that organisms such as bivalves ultimately experience (sensu Helmuth et al. 2010). An adequate characterization of coastal carbonate system variability is challenging owing to the inherent measurement issues and intensification of biological and geochemical processes at the land-ocean interface; even more challenging is relating this variability to the timing of sensitive life history stages of bivalves. Understanding the nature of such interactions in coastal waters represents a fundamental research problem for predicting ocean acidification effects on bivalves.

The frequency, magnitude, and duration of variability in carbonate chemistry that result in conditions crossing important thresholds for various levels of biological organization will ultimately determine biological responses in natural systems. We contend that the temporal frequency of processes that result in carbonate chemistry variability in the coastal zone overlain with the timescales of biological levels of organization and life history should provide the basis for a heuristic model useful for developing hypotheses (**Figure 2**).

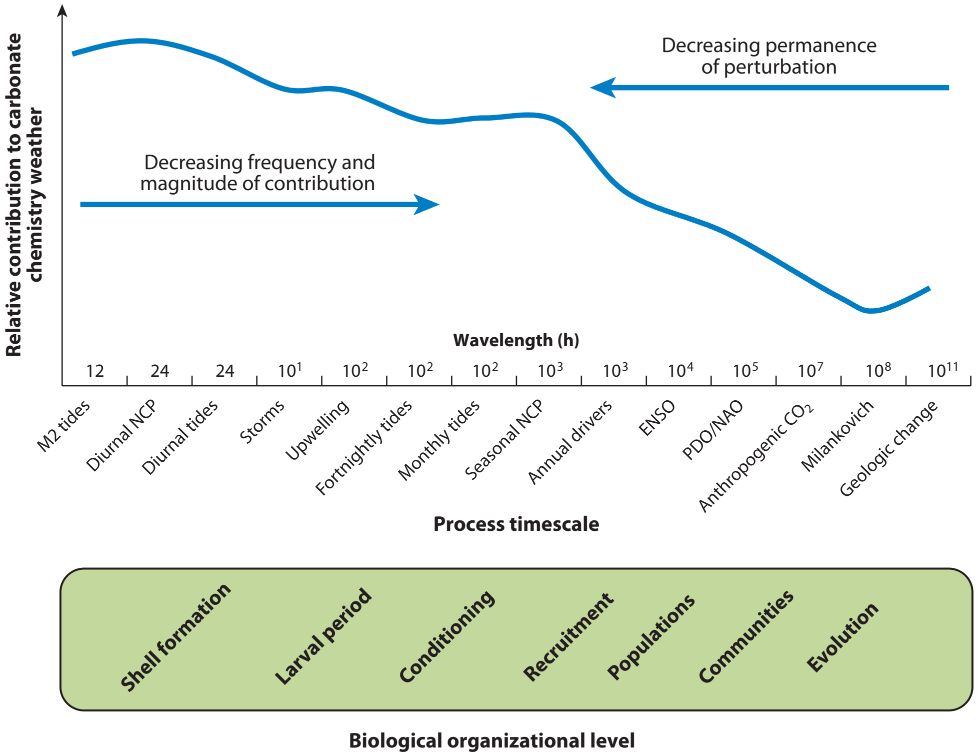

Figure 2

Conceptual model of carbonate weather timescales. The magnitudes of different processes contributing to localized carbonate weather (y axis) are plotted against the timescales over which those processes generally vary (x axis) in a hypothetical coastal habitat. The shape of this relationship likely varies among different coastal systems driven by different processes (tidal regime, freshwater inputs, light incidence, etc.). The numbers above the x axis are the approximate wavelengths, in hours, of the processes affecting carbonate chemistry, and the green box below the x axis highlights different levels of biological organization for a generic bivalve species. Importantly, the co-occurrence of these processes may amplify or dampen CO_2 variability in a given habitat. Processes occurring at shorter timescales can produce significant variability, but smaller perturbations to the long-timescale drivers would have more profound effects on higher levels of biological organization. We posit that adaptation potential and resilience are found at higher levels of biological organization, whereas acclimatization may occur on lower levels of biological organization. Anthropogenic CO_2 perturbation was taken from Zeebe (2012) and represents a return time after burning all known fossil fuel reserves. Although this is a relatively small contribution to the instantaneous carbonate weather, it represents an unparalleled perturbation of the marine carbonate system in the decades to centuries to come, and it does not include indirect effects on carbonate chemistry resulting from global change. Abbreviations: ENSO, El Niño–Southern Oscillation; NCP, net community production; PDO/NAO, Pacific Decadal Oscillation/North Atlantic Oscillation. “Milankovich” refers to the Earth’s climate sensitivity to orbital cycles.

Many recent reviews and syntheses have provided perspectives on organismal responses to acidification (e.g., Kroeker et al. 2010, Wicks & Roberts 2012, Gazeau et al. 2013, Parker et al. 2013). However, high-frequency data taken over timescales necessary to evaluate organismal responses within the context of the conceptual model are sparse. Below, we review the multiple processes that affect coastal carbonate chemistry, referring to marine bivalves as an example taxon affected by acidification over multiple timescales.

1.3. A Sense of Place: Life History Stages and Timescales of Marine Bivalves

Net community production (NCP): the ratio of total production to total respiration; here, we use it as an instantaneous (rather than temporally integrated) term

***p*CO$_2$:** partial pressure of CO$_2$, i.e., the amount of gaseous CO$_2$ dissolved in a mass of water or volume or air

Most benthic invertebrates have distinct pelagic and benthic stages corresponding to larval and adult periods, respectively. These Lagrangian and Eulerian lifestyles result in different chemical exposures for the larval and adult stages, which have different sensitivities and often differing levels of resilience to unfavorable carbonate chemistry. Larvae appear to be the most sensitive (Kurihara 2008, Salisbury et al. 2008a, Hettinger et al. 2012), with what seems to be increased sensitivity during initial shell formation (Barton et al. 2012, Waldbusser et al. 2013a) and then during metamorphosis to postlarval juveniles (Talmage & Gobler 2011). During the initial transition from larvae to juveniles, mortality and calcification are less affected by unfavorable chemistry with increasing size (Waldbusser et al. 2010). Although shell formation by adult bivalves tends to be sensitive to acidification effects (Gazeau et al. 2007, Thomsen et al. 2010), adults appear to be less sensitive than larvae.

Initial shell formation in bivalve larvae takes one to several days, similar to timescales of *M*2 tidal variability, diurnal net community production (NCP), and episodic events such as storms. Larvae then reside in the water column for a period of weeks to a month, corresponding to fortnightly (MF) and monthly (MM) tidal scales, upwelling events, and bloom dynamics (seasonal NCP). Following metamorphosis and movement to the benthos, postlarval juveniles take one to five years to grow and become reproductive, corresponding to annual and decadal scales in regional climate-scale processes such as the Pacific Decadal Oscillation, North Atlantic Oscillation, and El Niño–Southern Oscillation (**Figure 2**). Frequency distribution analyses of two month-long time series of *p*CO$_2$ (from Netarts Bay, Oregon, and the Piscataqua River inlet, New Hampshire) show distinct peaks at specific frequencies corresponding to tidal and diurnal periods (**Figure 3**). One strategy used during bivalve reproduction is the gradual release of gametes over the course of a spawning season, and there is some evidence that the spawning period becomes more concentrated in cooler, higher-latitude habitats (e.g., Shumway 1996). A more temporally diffuse, continuous supply of larvae would provide opportunities for success when conditions are favorable, even if

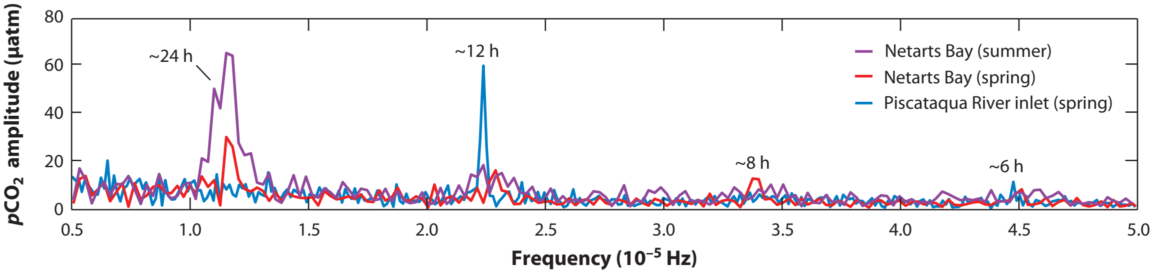

Figure 3

Frequency analysis of *p*CO$_2$ in two estuaries. The graph shows a fast Fourier transformation of *p*CO$_2$ data from Netarts Bay, Oregon (45.4°N, 123.9°W), and from the University of New Hampshire's Coastal Marine Laboratory at the Piscataqua River inlet (43.1°N, 70.7°W). The Netarts Bay data were measured March 1–31, 2011, and June 1–30, 2011; the Piscataqua River data were measured March 16–April 15, 2011. The predominant frequencies differed between the two estuaries, with near-daily variability dominating at Netarts Bay and *M*2 tidal variability dominating at the Piscataqua River inlet. Note also the differences in seasonal amplitude in Netarts Bay, highlighting a larger biological/chemical signal in summer months. This is likely due to upwelling-induced intensification of processes driving *p*CO$_2$ variability (i.e., nutrient and CO$_2$ delivery, light intensity, and net community production). A small 8-h frequency is visible in spring at Netarts Bay but appears in the noise during summer, and a strong 6-h signal (M2 tidal component) is visible in the Piscataqua River data. Given that these data sets were each one month long, we excluded the data below a frequency of 14 days, as this simply highlights the total *p*CO$_2$ variability over the one-month period. **Figure 4*b*** shows the entire record for Netarts Bay; it is important to note that, as can be seen there, the magnitude of the *y* axis is the amplitude of a given signal from the fast Fourier transformation, not the total range.

some larvae are lost during unfavorable periods, suggesting a greater risk of failure for populations with shorter, more concentrated spawning periods.

The pelagic and benthic life stages of larvae and adults, respectively, represent distinct habitats with potentially different carbonate weather that can be used to examine primary drivers of carbonate chemistry in these separate habitats. We do, however, recognize that this distinction is somewhat artificial, and that organisms experience carbonate weather that is influenced by both overlying water and the benthos.

2. PROCESSES AFFECTING PELAGIC CARBONATE CHEMISTRY

Increasing atmospheric CO_2 increases the partial pressure differential between air and sea, which facilitates CO_2 uptake in seawater. This may also facilitate more organic production in estuarine waters (Cai 2011), and thus more CO_2 may be captured as organic matter and eventually buried or respired. Coastal systems already experience the greatest range of NCP at multiple timescales (Gattuso et al. 1998), and it is unclear how these systems as a whole may respond to increasing CO_2. How an increasing CO_2 baseline would ultimately affect carbonate weather is one of many challenging research questions to address for coastal systems, especially because many systems differ both temporally and in their baseline conditions (Hofmann et al. 2011, Duarte et al. 2013) (**Figure 4**). In this section, we focus primarily on processes other than fossil fuel CO_2 that alter carbonate chemistry, but when possible will note how increasing atmospheric CO_2 may directly or indirectly affect these drivers.

An ongoing debate regarding the role of atmospheric CO_2 in estuaries has focused on whether estuaries can take up additional CO_2 given their already-elevated carbon from terrestrial inputs and production and respiration cycles (Borges & Gypens 2010, Cai 2011, Hunter et al. 2011). This is an important question, and its resolution will depend on high-temporal-resolution measurements and the integrated flux over seasonal cycles rather than on instantaneous measurements (e.g., Evans et al. 2011). As shown in **Figure 4**, pCO_2 in Netarts Bay fluctuates around 400 μatm from January to August; however, there are many periods when pCO_2 is high, and larvae show decreased growth and survival at these times. It is advantageous, then, that the native oysters in this region, *Ostrea lurida*, generally spawn before and after the summer upwelling system, in contrast to the typical hatchery production that occurs in summer. One recent strategy has been to begin hatchery production earlier in the year; however, there are ecological limitations for out-planted oyster seed and conditioning of spawning adults.

Terrestrial inputs into the coastal zone can have important impacts on carbonate chemistry. These chemical fluxes can directly alter carbonate chemistry by changing alkalinity, and can have indirect effects by providing nutrients that stimulate primary productivity (Section 2.1). The strong effects of biological production and respiration are among the largest drivers of variability in coastal carbonate chemistry (Section 2.2). Along eastern boundary upwelling systems, deep nutrient- and carbon-rich water is brought to the photic zone; these oceanic waters can be advected into coastal embayments, fueling NCP and altering chemistry (Section 2.3). Coupling between the ocean and atmosphere can be strong in coastal systems, as land-based sources can result in wet or dry deposition of bioactive constituents to waters (Section 2.4) and again create direct or indirect effects on carbonate chemistry.

2.1. Modulation of the Coastal Carbonate System by Freshwater Fluxes

Continental discharge of freshwater (3×10^5 km^3 annually; Fekete et al. 2001) can dramatically perturb the coastal carbonate system via chemical, biological, and physical changes over multiple

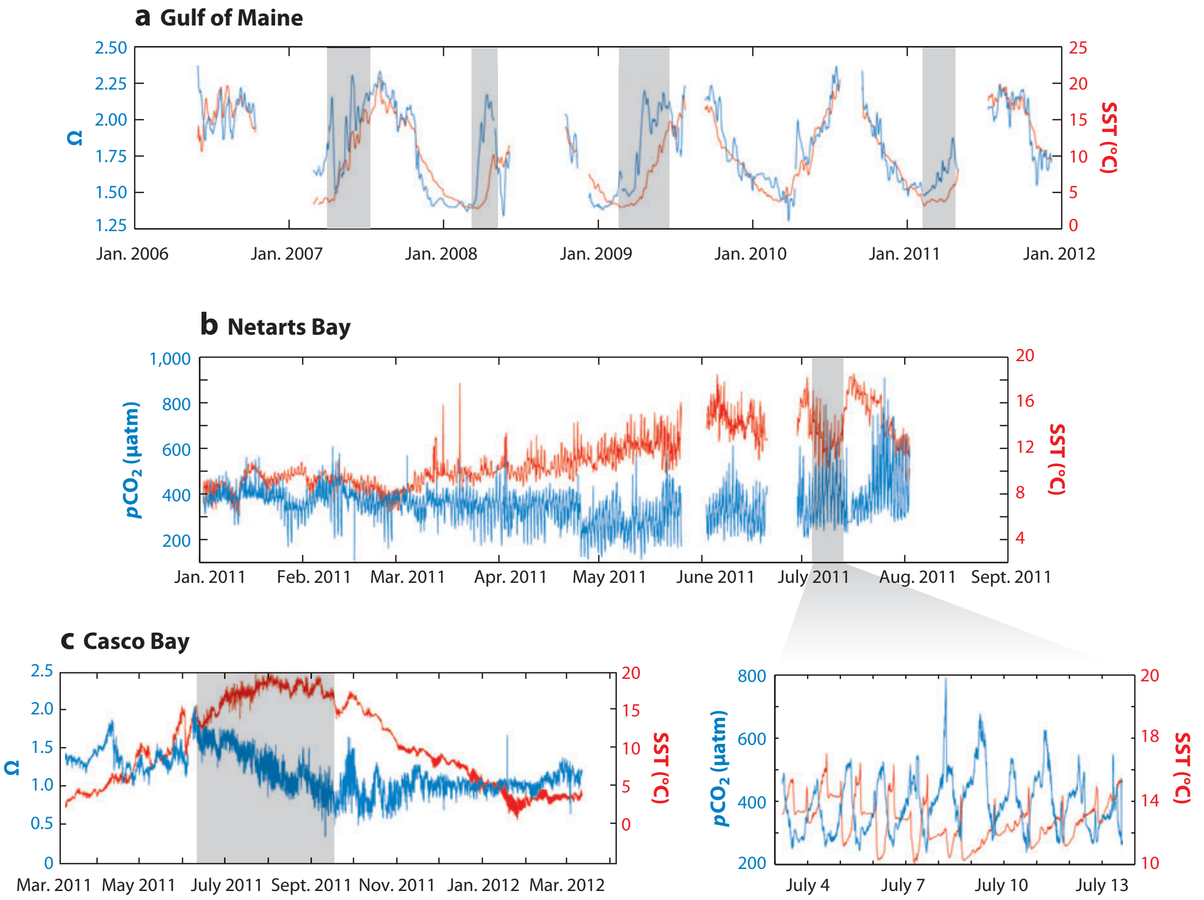

Figure 4

Time series of carbonate parameters. (*a*) Time series of saturation state (Ω) (±0.2) and sea-surface temperature (SST) from the University of New Hampshire's CO_2 buoy (43.0°N, 70.5°W) in the western Gulf of Maine. The data were captured every 1–3 h, and have been smoothed by 49 h to remove diurnal and M2 tidal effects. Note the first-order seasonal dependence of Ω on SST. The gray bars indicate times during which autotrophy (as inferred from decreasing pCO_2, not shown here) and increasing SST synergistically combine to increase Ω. (*b*) Time series of pCO_2 and SST in Netarts Bay, Oregon (45.4°N, 123.9°W), with a 1-min sample interval. The bay is similar to a coastal lagoon, with little freshwater input. Upwelling events lasting two to three weeks and followed by relaxation events are apparent in the June–August record. The inset shows the diurnal swings of several hundred microatmospheres of pCO_2 attributable to net community production. The bay also appears to be a CO_2 sink from approximately March until the spring transition around early June. Even during upwelling periods, the bay waters are sometimes well below atmospheric pCO_2 levels. (*c*) Time series of hourly Ω (±0.2) and SST (measured at 2-m depth) data from buoy DO2 (43.8°N, 70.0°W), operated by Bowdoin College and the University of Maine in Harpswell Sound, a semi-enclosed inlet within Casco Bay, Maine. High-frequency variability in Ω (often in excess of 0.4 units) is driven primarily by end-member mixing caused by the ∼3-m M2 tide, but also to a lesser degree by diurnal net community production. The gray bar indicates a seasonal trend of decreasing Ω as summer progresses. Note that Ω tends to increase as seawater warms and that this example runs counter to the observations in panel *a*. Such a trend implies a significant source of biological (respiratory) CO_2 driving Ω during this period.

timescales (Lohrenz & Cai 2006; Salisbury et al. 2008a, 2009). Some of the most profound and well-documented anthropogenic impacts on the coastal ocean from freshwater inputs result from landscape alterations (e.g., Seitzinger et al. 2005, Diaz & Rosenberg 2008, Aufdenkampe et al. 2011, Moser et al. 2012). Surface water fluxes to the coastal ocean carry rock-weathering products, including alkalinity (which is typically below oceanic concentrations), nutrients, and particulate and dissolved organic carbon. Weathering of carbonate and silicate minerals release inorganic carbon species into soil and stream water according to two simplified reactions,

Total alkalinity (TAlk): a measure of the buffering capacity of all of the conjugate bases of weak acids

$$\text{Carbonate: } CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$

and

$$\text{Silicate: } CaSiO_3 + 2CO_2 + 3H_2O = Ca^{2+} + 2HCO_3^- + H_4SiO_4,$$

and these weathering products alter coastal carbonate chemistry as they mix with seawater in estuarine environments (e.g., Salisbury et al. 2008a, Keul et al. 2010).

Weathering rates are inherently linked to soil formation, hydrology, water residence time, vegetation, slope, soil age, and soil and rock minerals as well as climate (Meybeck 1987, Nezat et al. 2004, Oh & Raymond 2006, Cai et al. 2008). Surface runoff is the primary driver of both chemical weathering rate (Kump et al. 2000, Eiriksdottir et al. 2011) and riverine chemical flux, with the largest fluxes to the coastal ocean occurring in midlatitude rivers (Cai et al. 2008). Seasonally increasing runoff dilutes total alkalinity (TAlk), effectively lowering saturation state (Salisbury et al. 2008a). **Figure 5** clearly shows the effects of dilution on saturation state and CO_3^{2-} in the Kennebec Estuary, Maine. Increased freshwater discharge over longer timescales can also dilute inorganic carbon constituents (Cai et al. 2008). In contrast, anthropogenic application of agricultural limestone over decadal timescales increases Ca^{2+} and carbonate alkalinity yield from watersheds (Raymond & Cole 2003, Raymond & Oh 2007), with river-water concentrations sometimes exceeding oceanic concentrations. Climate change scenarios have predicted an intensification of the hydrologic cycle, leading to a global increase in streamflow (Douville et al. 2002, Labat et al. 2004, Huntington 2006). However, other forecasts point to variable regional streamflow by midcentury (Milly et al. 2005, Aerts et al. 2006), coupled to significant effects on chemistry owing to land-use changes (Oh & Raymond 2006, Perrin et al. 2008). Global syntheses of coastal TAlk and DIC fluxes are emerging and will improve our understanding of freshwater effects on coastal acidification dynamics.

Numerous reviews have addressed the role of nutrient runoff in coastal systems and the many impacts this runoff has on estuarine and coastal ecosystems (Seitzinger et al. 2005, Diaz & Rosenberg 2008, Aufdenkampe et al. 2011, Moser et al. 2012). Given sufficient irradiance and residence time, nutrient runoff increases primary production (and subsequent respiration), perturbing carbonate weather at diurnal to seasonal frequencies, and perhaps longer. The alteration of the global nitrogen cycle through the production of fertilizers, legume cultivation, and combustion (Canfield et al. 2010) has greatly increased the flux of nitrogen to the coastal ocean (Caraco & Cole 1999, Green et al. 2004, Seitzinger et al. 2005). High population density and agricultural activity contribute to the largest fluxes of labile nitrogen occurring at midlatitudes (Green et al. 2004, Seitzinger et al. 2005), the same regions that have higher TAlk and DIC fluxes. How these drivers interact to alter carbonate chemistry will vary among regions and watersheds, but understanding the interactions is crucial to understanding regional coastal acidification impacts.

In the open ocean, carbonate speciation is the primary influence on TAlk; in coastal and freshwater systems, however, other acid-base pairs can contribute to TAlk and alter pH. Small changes in TAlk from noncarbonate sources can have significant effects on carbonate system

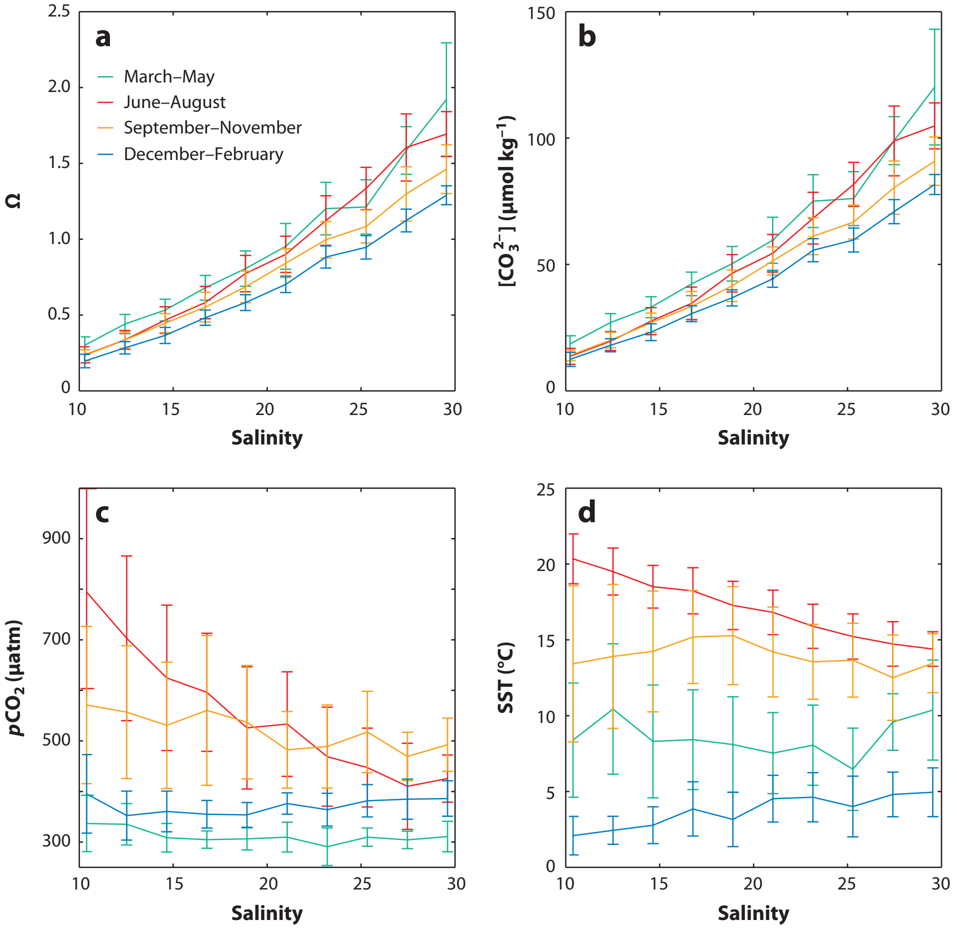

Figure 5

Carbonate parameters in the Kennebec Estuary, Maine (43.8°N, 68.8°W): (*a*) surface saturation state (Ω), (*b*) CO_3^{2-} concentration, (*c*) pCO_2, and (*d*) sea-surface temperature (SST). The data are from the University of New Hampshire's coastal transect database of 56 cruises from 2005 to 2009 (Salisbury et al. 2008a) and are averaged by season and salinity bin (2 psu). The Ω (±0.2) and CO_3^{2-} concentration (±2.1 µmol kg^{-1}) values are estimated from under-way salinity, temperature, pCO_2 (±3 µatm), and total alkalinity estimated from salinity (±12.6 µmol kg^{-1}). Note the dependence of both Ω and CO_3^{2-} concentration on salinity. The remainder of the variability arises from seasonal heating and cooling that affects CO_2 solubility and from net community production that consumes or produces CO_2.

speciation: For example, a 3 µmol kg^{-1} change in total phosphorus (a plausible perturbation in near-coastal waters) can result in a difference of 5–20 µatm in pCO_2. Fluxes of land-derived phosphorus and silicate vary widely in coastal waters (e.g., Crossland et al. 2001). The fraction of TAlk present as noncarbonate alkalinity is usually largest in river water and decreases upon mixing within the estuary. Dissolved organic matter contains weak organic acids (which therefore have strong conjugate bases) and associated alkalinity. The contribution of organic matter to alkalinity in river water can be as high as 100 µmol L^{-1} in the estuarine zone, where it can represent ~20% of TAlk at low salinity (Cai & Wang 1998) and can sometimes provide the dominant buffering capacity in river water (Hunt et al. 2011). This organic alkalinity may contribute as much buffering capacity as borate at higher salinities (Cai & Wang 1998). The noncarbonate alkalinity contributions to coastal zones are poorly constrained and represent a subject for future research.

2.2. Net Community Production in the Pelagic Zone

Production and respiration by plants, animals, and microbes in coastal waters represent two of the largest modulators of coastal carbonate chemistry (Sunda & Cai 2012) via the uptake and release of CO_2 (see seasonal and diurnal cycles in **Figure 4**). Addressing all of the drivers and dynamics of NCP in coastal waters is beyond the scope of this review, and several books and other reviews have adequately covered the topic (Alongi 1998, Gattuso et al. 1998, del Giorgio & Williams 2005). We therefore address some basic concepts germane to changing carbonate chemistry of coastal waters.

The NCP of organic carbon in marine waters has long been characterized by the well-known Redfield-Ketchum-Richards stoichiometry (respiration from left to right, and production the opposite):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \leftrightarrow 106CO_2 + 16NO_3^- + H_2PO_4^- + 17H^+ + 122H_2O.$$

The key effect on carbonate chemistry is the change in CO_2 concentration, but secondary effects are also notable. For simplicity's sake, we restrict the discussion here to the Redfield-Ketchum-Richards stoichiometry, although we acknowledge that the ubiquity of this ratio in the ocean has been challenged (e.g., Martiny et al. 2013). In the open ocean, nitrate (NO_3^-) is the dominant form of nitrogen available and thus taken up (e.g., Eppley & Peterson 1979), but ammonium (NH_4^+) is the preferred form of nitrogen for growth (Wheeler & Kokkinakis 1990). In eutrophic coastal systems, ammonium uptake can drive the majority of organic carbon generation (Xu et al. 2012). Nitrate assimilation and ammonium assimilation produce 1 mol of strong base and acid, respectively (Brewer & Goldman 1976), and thus a change in TAlk of approximately 0.16 times the magnitude of the DIC change. The production and release of dissolved organic matter can occur at a rate of 3–5 μmol L^{-1} per 200 μmol L^{-1} of production (Kim & Lee 2009) and thus can also increase alkalinity, as noted in Section 2.1. Again, however, the dominant driving force on the carbonate chemistry is the uptake and release of CO_2, thus changing the speciation of the carbonate system and pH. There is also a growing body of evidence that oceanic nitrogen (N_2) fixation is enhanced in tropical river plumes by diazotrophs (Subramaniam et al. 2008, Bombar et al. 2011). If this is a widespread phenomenon, it would represent an important nitrogen vector that plays a role in regulating net carbon fixation.

Estuarine and coastal waters can sustain high rates of particulate organic carbon production and DIC uptake (Cloern 2001, Kemp et al. 2005). Similar dynamics occur in river plumes of major and minor rivers (Cai 2003, Lohrenz & Cai 2006, Salisbury et al. 2008b, Hunt et al. 2010, Guo et al. 2012). Guo et al. (2012) reported that primary production in the mesohaline reaches of the Mississippi River plume increased TAlk by 50 μmol kg^{-1}, and Dai et al. (2008) observed that enhanced seasonal production in the Pearl River estuary lowered DIC (by 100–150 μmol kg^{-1}), increased pH (from 8.2 to 8.6), and increased TAlk (by 50 μmol kg^{-1}). However, net heterotrophy dominates many coastal regions (Smith & Hollibaugh 1997, Gattuso et al. 1998), increasing DIC (as CO_2) and lowering pH (see **Figure 4*c***). The effects of heterotrophy are pronounced in polluted systems (Frankignoulle et al. 1998, Guo et al. 2012) and those dominated by marsh input (Cai 2011). However, whether allochthonous organic carbon (dissolved and particulate) is respired in coastal waters depends on the lability of the carbon source (Hopkinson & Vallino 1995), with both the concentration and quality of organic matter influencing bacterial respiration rates (del Giorgio & Davis 2003, Rochelle-Newall et al. 2004).

One challenge for understanding the interaction of increasing atmospheric CO_2 levels and coastal production-respiration cycles will be to move beyond annual net assessments of carbon status and toward a better characterization of the short-term dynamics (sensu Evans et al. 2011). Strong seasonal and diurnal cycles in carbonate system parameters are evident in coastal areas (**Figure 4**), and biological processes are affected by temperature, timing of nutrient delivery, stratification, and a number of other well-understood processes. We suggest using high-time-resolution data sets and frequency analyses in various coastal systems to provide a diagnosis of drivers, as in **Figure 3**; these month-long data sets suggest a strong link between tidal and diurnal to seasonal cycles of NCP.

2.3. Upwelling

Production in surface waters results in sinking of particulate organic matter, a large portion of which is respired as it transits to the deep ocean. The expression of deep, upwelled water, rich with nutrients and carbon, fuels profitable fisheries along eastern boundary upwelling systems. Effects of upwelled water on coastal systems include enhanced net biological uptake of DIC, calcium carbonate dissolution/precipitation, and air-sea gas exchange (Hauri et al. 2009). Upwelling regions are important vectors for atmospheric carbon exchange via either productivity stimulated by upwelled nutrients (Hales et al. 2005, 2006) or high DIC fluxes that can routinely raise pCO_2 levels to >1,000 μatm (Evans et al. 2011, Fassbender et al. 2011, Hauri et al. 2013a). Although the net effects of upwelling on ecosystems can be seasonal, varying with the strength and direction of wind stress (Hales et al. 2005, Feely et al. 2010, Evans et al. 2011, Fassbender et al. 2011), event-scale dynamics often lasting roughly a fortnight play an important role in coastal ecosystems (Evans et al. 2011, Barton et al. 2012) and are visible in the June and July records of pCO_2 in Netarts Bay (**Figure 4*b***).

The intrusion of upwelled water has been implicated in coastal acidification (Hales et al. 2005; Feely et al. 2008, 2010; Fassbender et al. 2011; Mathis et al. 2012). Episodic intrusions of high-CO_2 upwelled water can reach estuarine regions, where this water becomes a significant factor in lowering the saturation state and pH (Feely et al. 2010, Barton et al. 2012, Mathis et al. 2012). The impact of upwelling on estuarine chemistry was recently demonstrated in Netarts Bay, where the hatchery production of Pacific oyster larvae is greatly reduced during strong upwelling periods (Barton et al. 2012).

2.4. Atmospheric Deposition

Atmospheric inputs of material affect carbonate dynamics either directly or via autotrophy stimulated by inorganic nitrogen. Sea-surface chemical dilution by rain is a well-known process that reduces near-surface salinity, TAlk, and DIC in proportion to the excess of precipitation over evaporation (Turk et al. 2010). Atmospheric inputs of sulfur and nitrogen arising from agriculture and combustion have half-lives of days to weeks (Doney et al. 2007), and thus the impact of deposition tends to be strongest in coastal regions (Paerl 1985, Doney et al. 2007, Hunter et al. 2011). How atmospheric fluxes influence the carbonate system depends on the chemical species deposited. Oxidation of nitrogen and sulfur compounds produces strong acids (HNO_3 and H_2SO_4) that completely dissociate in seawater. Deposition of ammonia increases or decreases TAlk, depending on whether the nitrogen deposited is wet (NO_3^-, acidic) or dry (NH_3, basic). Wet deposition of NH_4^+ is similar to NH_3 deposition, in that NH_4^+ in rainwater consumes a proton from water during its formation. Acidity levels in precipitation and river discharge in the northeastern United States have decreased in the past several decades owing to reduced sulfate emissions in North America as a result of regulations placed on coal-fired power plants (Clow & Mast 1999).

Atmospheric nitrogen fluxes also support considerable autotrophy in coastal waters. For example, Paerl et al. (2002) estimated that atmospheric nitrogen could support 15–33% of new productivity in the Neuse River estuary, North Carolina, and Mackey et al. (2010) estimated that it could support 9–20% of winter new productivity in Monterey Bay, California. Weekly storm events providing in excess of 1,000 μmol N m^{-2} d^{-1} have been reported in coastal waters (Jordan & Talbot 2000), and these events were also associated with increased chlorophyll biomass.

3. PROCESSES AFFECTING BENTHIC CARBONATE CHEMISTRY

The sediment-water interface in coastal habitats is where settling bivalve larvae make the transition to adult stages and then generally reside for the rest of their lifetimes. Different bivalves (e.g., mussels, clams, oysters) show strong selection preferences for general habitat types and specific properties within their habitats (e.g., Butman 1987, Green et al. 2013). We focus this discussion on sediment habitats where strong geochemical gradients exist between the seafloor and overlying waters.

Sediment habitats, and in particular depositional sites, receive particulate organic and inorganic carbon from the overlying water and may either bury or rerelease carbon on timescales slower than that of the depositional event, thus functioning like a capacitor. Hansen & Blackburn (1992) estimated that when organic matter from a phytoplankton bloom in the overlying water is deposited on the sediment, rapid respiration results in an organic carbon half-life of two to three weeks. In addition, in areas where light reaches the bottom, coastal marine sediments may be sites of strong primary production from benthic algae (MacIntyre et al. 1996, Gattuso et al. 2006). Respiration and nutrient regeneration (Rowe et al. 1975, Kristensen 1993), dissolution or formation of calcium carbonate (Green & Aller 1998, 2001), and tidal pumping and groundwater efflux (Le Hir et al. 2000, Burnett et al. 2003) are all important in the coastal zone. The heterogeneous and dynamic nature of benthic habitats makes broad generalizations difficult, and here we discuss only the general aspects of the cycling of organic carbon (Section 3.1), calcium carbonate (Section 3.2), and tidal exchanges (Section 3.3). In habitats where benthic-pelagic coupling is strong, bivalves may increase this coupling via filter feeding and by deposition of organically rich biodeposits (Newell 2004). We highlight coupled time-series data from the Gulf of Maine that show the concurrent and opposite changes in carbonate chemistry during the summer stratification and bloom (**Figure 6**). Myriad other factors also determine the success of bivalve populations in these sediment habitats, but addressing these in conjunction with coastal carbonate chemistry is beyond the scope of this review.

3.1. Benthic Cycling of Organic Matter

As noted above, several excellent books and reviews have covered coastal production and respiration (Alongi 1998, Gattuso et al. 1998, del Giorgio & Williams 2005); here, we highlight important aspects of these processes in the benthos and their timescales of variability in relation to the benthic stages of bivalves. Coastal marine sediments are sites of significant organic matter cycling (e.g., del Giorgio & Williams 2005) owing to high production rates in overlying waters, shallow water columns supporting benthic primary production, rapid deposition of fresh organic matter, and high nutrient availability. Within estuaries, roughly 24% of the total organic input

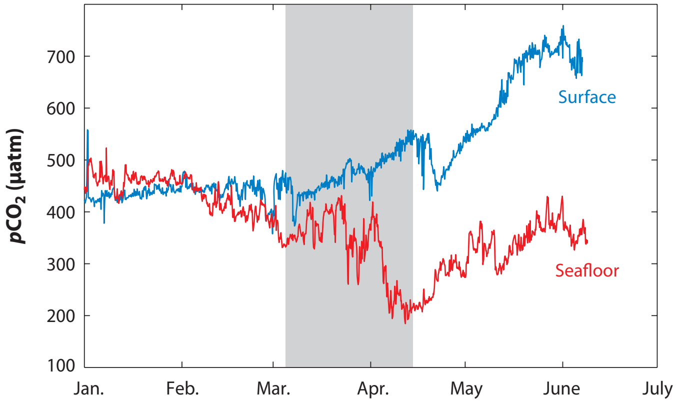

Figure 6

Benthic-pelagic coupling of pCO_2 in the western Gulf of Maine in 2012. pCO_2 at the surface is from the University of New Hampshire's CO_2 buoy (43.0°N, 70.5°W); pCO_2 near the bottom (±5 µatm, estimated) was taken 4 m above the seafloor (90-m depth) near Stellwagen Bank (42.3°N, 70.5°W). The spring bloom of phytoplankton in the surface waters results in a drawdown of surface pCO_2 and concurrent increase in deepwater pCO_2 as the bloom products (particulate organic matter) sink. The gray bar shows a period of increasing production in surface waters and respiration in deep water. This suggests a close coupling in time between net autotrophy at the surface and net respiration in deep water.

is respired by sediments (Hopkinson & Smith 2005), with significant variability among different estuarine systems.

Importantly, although this percentage of respiration input in benthic habitats seems small relative to that of pelagic habitats, much of this respiration is spatially compressed in the upper few millimeters or centimeters of sediment (Glud 2008), thus concentrating CO_2 to a space just slightly larger than that of settling bivalves. Below this surface layer of aerobic respiration, suboxic microbial metabolisms such as denitrification and sulfate reduction use other terminal electron acceptors to oxidize organic matter. Suboxic metabolisms also produce CO_2 but in some cases increase alkalinity (Soetaert et al. 2007), thereby countering some of the CO_2 effect. Pore-water profiles showing increasing saturation state of calcium carbonate minerals with depth below the oxic sediment layer are well documented in temperate siliceous sediments (Green & Aller 1998). Burrowing bivalves must retain contact with overlying waters for oxygen and often for feeding, and they do this through their siphons. Many species reside at depth in sediment, presumably to avoid predation. Upon settlement, many bivalves usually lack fully formed siphons and so must remain in the upper oxic layer until siphons form. Once the siphons grow long enough to burrow more deeply, their shells may be exposed to less corrosive conditions owing to the alkalinity generation often seen in deeper anoxic sediment layers.

In many organic-rich habitats, suboxic metabolisms may also occur near the sediment-water interface and alter chemistry in nonintuitive ways. For example, Green & Aller (1998) showed that the sediment calcium carbonate saturation state is more thermodynamically favorable in summer owing to the dominance of anaerobic metabolism and storage of the reduced metabolites. Conversely, conditions become undersaturated in the winter owing to the dominance of aerobic metabolism and reoxidation of stored anaerobic metabolites (Green & Aller 1998). Interestingly, the recruitment of calcifying benthic foraminifera corresponds with the end of the spring bloom in these sediments (Green et al. 1993) and highlights the possible importance of settlement timing for bivalves relative to sediment chemistry conditions.

Respiration in nearshore sediments is driven by the supply of organic matter, transport dynamics of electron acceptors for respiration, and other environmental variables such as temperature and light (in photic sediments). Although the example above (Green & Aller 1998) suggests that anaerobic metabolism can have beneficial effects, metabolites from these respiration pathways (e.g., sulfides) are often toxic. Therefore, very high levels of sediment organic matter typically exclude megafauna. The presence of oxygen (in conjunction with organic substrate) is a strong control on the saturation state of sediment pore waters. In sediments within the photic zone, benthic primary producers can generate significant amounts of oxygen and take up CO_2 (MacIntyre et al. 1996), although few studies have captured the diurnal-scale variability in the surface sediment carbonate chemistry. Wenzhöfer & Glud (2004) found strong diurnal fluctuations in sediment pore-water oxygen, ranging from approximately 20% to 180% oxygen saturation, as a result of benthic primary production in the upper centimeter of sediment. Obtaining high-frequency data on sediment pore-water chemistry remains a technical challenge, but the development of new approaches (Zhu et al. 2005) will certainly provide insights into the magnitude of change in these bivalve habitats in the near future.

3.2. Calcium Carbonate Cycling

Calcium carbonate cycling in marine sediments is strongly coupled to respiration of organic matter. Emerson & Bender (1981) recognized the importance of metabolic dissolution of calcium carbonate in the deep ocean, and more recently dissolution in temperate, nearshore, siliceous sediments with supersaturated overlying water has been documented (Green & Aller 1998, 2001). Much effort has focused on calcium carbonate sedimentary systems (e.g., Morse & Mackenzie 1990, Andersson et al. 2006). The role of siliceous and terrigenous sediment habitats in calcium carbonate cycling is still poorly quantified, in terms of both authigenic mineral formation and the contribution from calcium carbonate–shelled organisms. Krumins et al. (2013) used a one-dimensional reaction-transport model to estimate alkalinity fluxes in coastal ocean sediments (excluding photic sediments) and found that dissolution of calcium carbonate was responsible for approximately half the effective alkalinity flux out of these shallow-water dark sediments. The rest is attributable to suboxic metabolisms that generate alkalinity either directly or through other secondary reactions. Alkalinity produced in sediments with benthic primary production has not been as well constrained.

Bivalves can produce significant amounts of calcium carbonate in temperate coastal zones, resulting in significant accretions of calcium carbonate shell (e.g., Coen & Grizzle 2007). Chauvaud et al. (2003) estimated that clam growth in San Francisco Bay, California, produces upward of 1 kg $CaCO_3$ m^{-2} y^{-1}. Although echinoderms are a different taxon, Lebrato et al. (2010) estimated that their calcification along continental shelves produces ~0.86 Pg $CaCO_3$ y^{-1}, with a stock of ~2.11 Pg $CaCO_3$. The extent to which shells are preserved or dissolve is quite variable (Reaves 1986, Walker & Goldstein 1999, Powell et al. 2011) and depends on rates of anaerobic respiration that generate alkalinity and on length of time in the taphonomically active zone (Tomašových et al. 2006, Powell & Klinck 2007, Waldbusser et al. 2013b). Recent estimates of oyster shell degradation on intact oyster reefs estimated shell half-lives of roughly several years to a decade (Powell & Klinck 2007), and these estimates were corroborated by laboratory studies of shell dissolution rates (Waldbusser et al. 2011a).

The production and concentration of organic-rich biodeposits and calcium carbonate shells by filter-feeding bivalves provide the potential for a calcium carbonate counterpump in these habitats (Waldbusser et al. 2013b). The regeneration of alkalinity in these habitats may therefore be an important mechanism to create conditions that are more locally favorable for settling larvae. The feedbacks in these shell-aggregating habitats are not well characterized, nor are the alkalinity fluxes from photic, organic-rich sediments containing abundant calcium carbonate shells.

Numerous studies have measured alkalinity fluxes in shelf and deep-sea sediments (e.g., Emerson et al. 1984, Jahnke & Jahnke 2004), and some recent efforts have begun filling gaps regarding shallow sediments (Faber et al. 2012). As noted above, however, organic-rich, shelly habitats may also function as a capacitor in removing and then slowly regenerating alkalinity. Recent field and laboratory studies have highlighted the importance of a higher saturation state for settling clam larvae (Green et al. 2013), and therefore it seems likely that the interplay of organic matter and shell formation would have important impacts on bivalve recruitment.

3.3. Tidal Pumping and Groundwater Discharge

Advective inputs of water, either from tidal flats and marshes or from groundwater sources, are underappreciated and likely important controls on carbonate chemistry in shallow-water systems. Although Odum suggested the "outwelling" hypothesis several decades ago (see Odum 2002), most work in this area has focused on organic carbon or nutrient delivery from these habitats. During each tidal cycle, intertidal areas are inundated and then drain if the sediment is permeable to flow. Recent estimates by Cai (2011) have highlighted the importance of organic inputs to estuaries from marsh environments; these inputs result in an annual average net CO_2 release from inner estuaries. However, timescales of variability in carbonate chemistry caused by tidal pumping and seasonal hydrological changes relative to the timing of recruitment events and seasonal spawning will determine the importance of these processes in coastal acidification (**Figures 2** and **3**). In these outwelling systems, inputs to the local waters are generally believed to create less favorable carbonate chemistry conditions. Other examples of these types of inputs have been described in several recent papers about oyster population responses to outflows from acid sulfate soils (e.g., Dove & Sammut 2007). We believe that these tidal influences on sediment pore-water exchange are probably underrepresented components of variability in coastal carbonate chemistry.

Only in the past decade has submarine groundwater discharge received attention as an important biogeochemical process in coastal waters (Moore 2010). The hydraulic head from groundwater can force freshwater through aquifers and result in subterranean estuaries where groundwater and seawater mix (Burnett et al. 2003, Kroeger & Charette 2008). Several excellent reviews have addressed this topic (e.g., Santos et al. 2012); we note only that some groundwaters have exceptionally high alkalinity and can result in significant efflux to coastal waters (Nascimento et al. 1997). These fluxes could plausibly result in localized interactions between groundwater and benthic fauna (e.g., Dale & Miller 2008), although we are not aware of any studies that have identified this phenomenon with calcifiers. These processes are likely to cause fluctuations on the scales of tidal cycles to decades, with the latter possibly linked to variations in aquifer levels due to changing rainfall (recharge) and extraction rates.

4. HABITAT-SPECIFIC DYNAMICS

In this section, we briefly synthesize possible acidification impacts in three nearshore habitats (the Arctic coast, seagrasses, and shell aggregations) where carbonate chemistry conditions will likely depart significantly from a global average, show decoupling of carbonate system parameters, be affected by changing climate, and respond differently to increasing baseline CO_2. Many environmental factors are relevant to coastal habitats, but to simplify and constrain the current treatment, we consider only the acidification impacts. Other temperate shallow systems, including kelp beds, mud and sand flats, and rocky intertidal zones, could also have significant responses to acidification.

4.1. The Arctic

A strong seasonal freeze-melt cycle and a concentrated seasonal NCP peak in the Arctic suggest vulnerability to coastal acidification. Calcifying marine organisms are already vulnerable to ocean acidification in these cold waters (Bates & Mathis 2009, Fabry et al. 2009), as lower temperatures increase the solubility of CO_2. TAlk and DIC are variable in freeze-melt cycles owing to brine rejection during ice formation (Rysgaard et al. 2007). Nevertheless, the contribution of melting ice typically promotes an undersaturation of calcium carbonate minerals (Rysgaard et al. 2007, Yamamoto-Kawai et al. 2009, Mathis et al. 2011). Fluvial inputs to the Arctic will continue to dilute TAlk and DIC in coastal regions (Salisbury et al. 2008a), serving as a precondition for coastal acidification. High rates of primary production can increase pH and saturation state in surface waters (Bates & Mathis 2009; Mathis et al. 2010, 2011). However, the decoupling of productivity and grazing in the Arctic (e.g., Lavoie et al. 2010) increases organic matter export to the benthos, which promotes high CO_2 production in benthic environments while supplying food for commercially important fish and marine mammals dependent on robust bivalve populations.

Climate change is already affecting the way the Arctic hydrological cycle functions (Peterson et al. 2006), leading to increased Arctic precipitation and river discharge (McClelland et al. 2004), earlier annual ice/snow melt (Lammers et al. 2007), and increased permafrost melt (Camill 2005). Recent observations have shown that the maximum summer sea ice extent in the Arctic has decreased by more than 20% over the past three decades (Cavalieri et al. 2003), with thinning in several parts of the Arctic Ocean (Wadhams & Davis 2000). Although decreased ice extent may increase mixing and upwelling and promote increased productivity (Arrigo et al. 2008), this effect may be dampened owing to buoyancy from higher freshwater discharge. Likewise, CO_2 drawdown from new productivity stimulated by increased flux of limiting nutrients from land could be offset by CO_2 production stimulated by increased flux or lability of terrestrial organic carbon. These and other community metabolism changes may alter surface ecosystem structure, benthic-pelagic coupling (Arrigo et al. 2008), particle export, and the air-sea carbon flux (Shadwick et al. 2011). In combination, these effects will likely significantly alter carbonate weather.

4.2. Seagrass

Seagrass ecosystems are ecologically important habitats (Orth et al. 1984) and have been diminished in many coastal areas (Duarte 2002). Several bivalve species show strong habitat association with seagrasses (Peterson & Heck 2001), and Marinelli & Waldbusser (2005) noted that seagrass-animal associations appeared to be strongest under stressful conditions. Seagrasses grow more rapidly under elevated CO_2 (Zimmerman et al. 1997, Unsworth et al. 2012) and have strong local effects on carbonate chemistry (Manzello et al. 2012). However, recent work has shown that elevated CO_2 leads to decreases in protective phenolic compounds that normally help protect seagrasses against grazing (Arnold et al. 2012), thus making them more susceptible to consumers and potentially reducing localized benefits. Given the global impact of seagrass ecosystems on carbon sequestration (Fourqurean et al. 2012), there continues to be strong interest in these habitats as acidification refugia for sensitive species (as in corals; Manzello et al. 2012). Seasonal and daily NCP cycles result in uptake and release of CO_2 that could have either positive or negative effects on bivalves outside of the net or average condition. Increasingly unfavorable carbonate chemistry could be mitigated within and near seagrass meadows owing to their daytime/growing season carbon uptake. Alternatively, the increasing CO_2 baseline shift might result in compounding of nighttime respiration/winter decay releases, pushing the marine carbonate system past important organismal thresholds. It is unclear whether additional grazing pressure on seagrasses under higher CO_2 (Arnold et al. 2012) will alter carbonate chemistry within seagrass habitats on time and space scales important to bivalves. Although many seagrass-sediment carbon studies have been conducted in carbonate sands, biogeochemical variability in terrigenous sediments may be larger (e.g., Erftemeijer & Herman 1994), and hydrodynamics will be an important covariate (Koch & Gust 1999). In terms of impacts on bivalves, an important consideration is therefore the timing of settlement in conjunction with the diurnal and seasonal cycles of carbonate chemistry within these habitats.

4.3. Shell Aggregations

Many calcium carbonate–forming organisms appear to have gregarious settlements, and, in particular, many bivalve species appear to prefer habitats that have intact shell material (Bayne 1969). These shell-aggregating bivalve species are also found in lower-salinity environments. Kidwell & Jablonski (1983) clearly articulated the concentrating of calcium carbonate by these organisms, and Gutiérrez et al. (2003) well summarized the ecological significance of shelly habitats. Although little work has been done on the alkalinity cycling and carbon biogeochemistry of shell aggregations (as noted in Section 3.2, above), several investigators have considered shell cycling (Tomašových et al. 2006, Powell & Klinck 2007, Powell et al. 2011). For many bivalve species, filter feeding results in organic-rich biodeposits in close association with the shelly sediments in which these organisms reside. In the case of oysters, this provides the possibility of an oyster reef carbonate pump, as suggested by Waldbusser et al. (2013b), which would regenerate alkalinity and potentially elevate the saturation state at settlement sites. How these calcium carbonate–concentrating habitats alter embayment and habitat carbonate chemistry is poorly constrained (Chauvaud et al. 2003, Waldbusser et al. 2013b). Additionally, seasonal growth patterns and temperature would likely create significant variability in alkalinity and carbon fluxes within each year, and how the strength of fluxes may vary with settlement timing is unknown.

SUMMARY POINTS

1. In coastal waters, the intersection of biological and geochemical processes results in a complex pattern of carbonate chemistry that varies over multiple timescales. The interaction of these various processes can amplify or compress carbonate chemistry variability. One framework for addressing the impact of global changes in atmospheric CO_2 on coastal ecosystems is to distinguish between carbonate weather and climate (where weather is the short-term variability and climate is the longer-term shift in the baseline).
2. The effects of climate change are most pronounced in the changes in frequency, magnitude, and duration of events that cross important thresholds for different levels of biological organization, from organisms to species persistence. We therefore should be looking at the extreme carbonate chemistry events as important drivers of species persistence or failure in a high-CO_2 world.

3. Coastal zones receive significant terrestrial fluxes that alter the carbonate weather across different timescales. Because there can be independent processes that change total alkalinity (conservative mixing) and acid-base reactions (e.g., net community production, CO_2 exchange), carbonate chemistry may be decoupled in the coastal zone. For example, a decrease in calcium carbonate saturation state from riverine dilution would be possible without direct changes in acid-base chemistry. However, dilution is often accompanied by riverine subsidies of organic matter that can fuel net respiration or by limiting nutrients that fuel net autotrophy.
4. Many organisms have distinct life history stages in which they reside either in the water column or in the benthos; these distinct stages have different sensitivities to poor carbonate chemistry and are affected to varying degrees by pelagic and benthic processes. Therefore, it is important to characterize the contributions of both pelagic and benthic processes to coastal carbonate chemistry.
5. How carbonate chemistry will change within specific habitats is currently difficult to assess, particularly in terms of how those changes may ultimately affect the organisms residing there. Improving our ability to predict coastal acidification impacts will require a coupled approach of characterizing and understanding the many processes affecting carbonate chemistry and performing carefully designed experiments.

FUTURE ISSUES

1. Efforts should be made to determine the relative impacts of various coastal carbonate chemistry drivers and how these may intersect to create the carbonate weather. Significant research has already been done in many habitats and should provide a starting point for developing hypotheses about budgeting of carbonate and noncarbonate constituents that affect the acid status of coastal waters. An important question is whether increasing CO_2 simply shifts the baseline or also results in nonlinear effects such as greater variability at different frequencies. Additionally, measurements of coastal and estuarine carbonate chemistry are challenging, and sufficient technical expertise is needed to provide the appropriate tools and standards necessary to accurately perform these measurements.
2. Future monitoring efforts should be geared toward both open-ocean chemistry and nearshore dynamic systems, as the weather patterns in carbonate chemistry are just beginning to come to light. Ensuring that these chemical monitoring efforts are in place during important seasonal periods for organisms seems fruitful.
3. Monitoring benthic biogeochemical dynamics at the resolution that water column measurements are now being made is a technologically challenging but important component to understanding coastal acidification.
4. Linking experimental studies of species responses to realistic carbonate chemistry conditions from within these species' habitats will help illuminate the potential impacts of a shifting baseline. Studies that can address both short-term acclimation in organisms and long-term adaptation potential in populations and species are also important.

5. Although our observational capacity has grown during the past decade, a global synthesis of coastal carbonate processes, particularly those at high frequency, is still lacking owing to instrument and technical needs.

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