Impacts of ocean acidification on marine fauna and ecosystem processes

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Oceanic uptake of anthropogenic carbon dioxide (CO_2) is altering the seawater chemistry of the world's oceans with consequences for marine biota. Elevated partial pressure of CO_2 (pCO_2) is causing the calcium carbonate saturation horizon to shoal in many regions, particularly in high latitudes and regions that intersect with pronounced hypoxic zones. The ability of marine animals, most importantly pteropod molluscs, foraminifera, and some benthic invertebrates, to produce calcareous skeletal structures is directly affected by seawater CO_2 chemistry. CO_2 influences the physiology of marine organisms as well through acid-base imbalance and reduced oxygen transport capacity. The few studies at relevant pCO_2 levels impede our ability to predict future impacts on foodweb dynamics and other ecosystem processes. Here we present new observations, review available data, and identify priorities for future research, based on regions, ecosystems, taxa, and physiological processes believed to be most vulnerable to ocean acidification. We conclude that ocean acidification and the synergistic impacts of other anthropogenic stressors provide great potential for widespread changes to marine ecosystems.

Keywords: anthropogenic CO_2, calcification, ecosystem impacts, hypercapnia, ocean acidification, physiological effects, zooplankton.

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Introduction

Rising atmospheric carbon dioxide (CO_2) concentration is causing global warming and ocean acidification (Caldeira and Wickett, 2003, 2005; Feely *et al.*, 2004; Orr *et al.*, 2005), which increasingly are recognized as important drivers of change in biological systems (Lovejoy and Hannah, 2005). For at least 650 000 years prior to the industrial revolution, atmospheric CO_2 concentrations varied between 180 and 300 ppmv (Siegenthaler *et al.*, 2005). As a result of human activity, today's atmospheric CO_2 concentration is 380 ppmv and currently is rising at a rate of $\sim$0.5% year^{-1} (Forster *et al.*, 2007), which is $\sim$100 times faster than any change during the past 650 000 years (Royal Society, 2005; Siegenthaler *et al.*, 2005). Approximately one-third of the anthropogenic CO_2 produced in the past 200 years has been taken up by the oceans (Sabine *et al.*, 2004). The global ocean inventory of anthropogenic carbon was 118 ± 19 Pg C in 2004 (Sabine *et al.*, 2004), which can be adjusted upwards to 140 Pg C in 2005 based on Denman *et al.* (2007, Table 7.1). Without this ocean sink, the anthropogenic change in atmospheric CO_2 concentration would be 55% higher than the observed change from 280 to 380 ppmv (Sabine *et al.*, 2004). Although oceanic uptake of anthropogenic CO_2 will lessen the extent of global warming, the direct effect of CO_2 on ocean chemistry may affect marine biota profoundly.

Elevated partial pressure of CO_2 (pCO_2) in seawater (also known as hypercapnia) can impact marine organisms both via decreased calcium carbonate ($CaCO_3$) saturation, which affects calcification rates, and via disturbance to acid–base (metabolic) physiology. Recent work indicates that the oceanic uptake of anthropogenic CO_2 and the concomitant changes in seawater chemistry have adverse consequences for many calcifying organisms, and may result in changes to biodiversity, trophic interactions, and other ecosystem processes (Royal Society, 2005; Kleypas *et al.*, 2006). Most research has focused on tropical coral reefs and planktonic coccolithophores. Little information is available for other important taxa, for processes other than calcification, or for potential ecosystem-level consequences emerging from the oceanic pCO_2 levels that are predicted to occur over the next 100 years. Here we discuss the present and projected changes in ocean carbonate chemistry, and assess their impacts on pelagic and benthic marine fauna and ecosystem processes. We exclude corals from this discussion, but note that excellent recent reviews on this topic exist (Langdon and Atkinson, 2005; Guinotte *et al.*, 2006; Kleypas and Langdon, 2006). We highlight many of the gaps in our knowledge and identify critical questions for future research.

The ocean's inorganic carbon system: present and future changes

The CO_2–carbonate system in seawater

The inorganic carbon system is one of the most important chemical equilibria in the ocean and is largely responsible for controlling the pH of seawater. Dissolved inorganic carbon (DIC) exists in

	Glacial	Pre-industrial	Present	2XCO$_2$	3XCO$_2$	Change from pre-industrial to 3XCO$_2$
$CO_{2\,(g)}$						
pCO_2	180	280	380	560	840	200%
Gas exchange						
$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_3$ Carbonic acid	7	9	13	18	25	178%
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ Bicarbonate	1666	1739	1827	1925	2004	15%
$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ Carbonate	279	222	186	146	115	- 48%
DIC	1952	1970	2026	2090	2144	8.8%
$pH_{(sws)}$	8.32	8.16	8.05	7.91	7.76	- 0.4
$\Omega_{calcite}$	6.63	5.32	4.46	3.52	2.77	- 48%
$\Omega_{aragonite}$	4.26	3.44	2.90	2.29	1.81	- 47%

Figure 1. Concentrations of carbon species (in units of μmol kg^{-1}), pH values, and aragonite and calcite saturation states of average surface seawater for pCO_2 concentrations (ppmv) during glacial, preindustrial, present day, two times pre-industrial CO_2, and three times pre-industrial CO_2. Changes in the inorganic carbon system were computed by assuming equilibrium with atmospheric CO_2, assuming PO_4 = 0.5 μmol l^{-1} and Si = 4.8 μmol l^{-1}, and using the carbonic acid dissolution constants of Mehrbach *et al.* (1973) as refitted by Dickson and Millero (1987). pH is based on the seawater scale. The last column shows the changes from the pre-industrial levels to three times atmospheric CO_2 (modified from Feely *et al.* (2004) and Kleypas *et al.* (2006)).

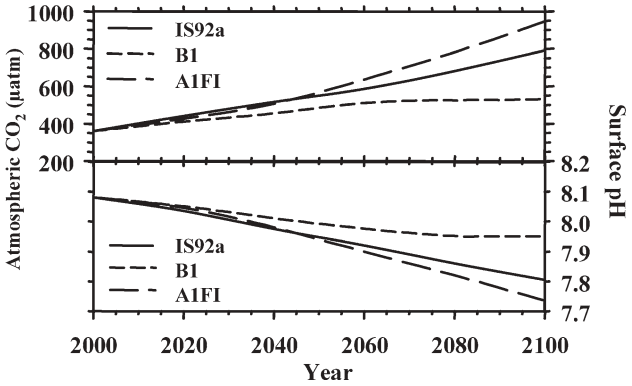

Figure 2. Atmospheric CO_2 concentration projected under the IS92a "business-as-usual" IS92a CO_2 emissions scenario, bounded by the most and least conservative SRES scenarios, B1 and A1F1, respectively, and projected global average surface seawater pH (modified from Meehl *et al.* (2007)).

seawater in three major forms: bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}), and aqueous carbon dioxide ($CO_{2(aq)}$), which here also includes carbonic acid (H_2CO_3). At a pH of 8.2, ~88% of the carbon is in the form of HCO_3^-, 11% in the form of CO_3^{2-}, and only ~0.5% of the carbon is in the form of dissolved CO_2. When CO_2 dissolves in seawater, H_2CO_3 is formed (Figure 1). Most of the H_2CO_3 quickly dissociates into a hydrogen ion (H^+) and HCO_3^-. A hydrogen ion can then react with a CO_3^{2-} to form bicarbonate. Therefore, the net effect of adding CO_2 to seawater is to increase the concentrations of H_2CO_3, HCO_3^-, and H^+, and decrease the concentration of CO_3^{2-} and lower pH ($pH = -\log[H^+]$). These reactions are fully reversible, and the basic thermodynamics of these reactions in seawater are well known (Millero *et al.*, 2002). The atmospheric CO_2 value today is ~100 ppmv greater than the pre-industrial value (280 ppmv), and the average surface ocean pH has dropped by 0.1 unit, which is about a 30% increase in $[H^+]$. Under the IPCC emission scenarios (Houghton *et al.*, 2001), average surface ocean pH could decrease by 0.3–0.4 pH units from the pre-industrial values by the end of this century (Caldeira and Wickett, 2005; Figure 2).

Present and future changes in carbonate saturation

The reaction of CO_2 with seawater reduces the availability of carbonate ions that are necessary for marine calcifying organisms, such as corals, molluscs, echinoderms, and crustaceans, to produce their $CaCO_3$ shells and skeletons. The extent to which such organisms are affected depends largely upon the $CaCO_3$ saturation state (Ω), which is the product of the concentrations of Ca^{2+} and CO_3^{2-}, divided by the apparent stoichiometric solubility product (K_{sp}^*) for either aragonite or calcite, two types of $CaCO_3$ commonly secreted by marine organisms:

$$\Omega = [Ca^{+2}][CO_3^{2-}]/K_{sp}^*, \quad (1)$$

where the calcium concentration is estimated from the salinity, and $[CO_3^{2-}]$ is calculated from DIC and total alkalinity (TA) measurements (Feely *et al.*, 2004). Increasing CO_2 concentrations in the atmosphere, and thus in the surface ocean, will continue to decrease the $[CO_3^{2-}]$ in the upper ocean, thereby lowering $CaCO_3$ saturation levels by means of the reaction:

$$CO_2 + CO_3^{2-} + H_2O = 2HCO_3^-. \quad (2)$$

In regions where Ω_{arag} or Ω_{cal} is >1.0, the formation of shells and skeletons is favoured. For values <1.0, seawater is corrosive to $CaCO_3$ and, in the absence of protective mechanisms (e.g. Corliss and Honjo, 1981; Isaji, 1995), dissolution will begin. Saturation states are generally highest in the tropics and lowest in the high latitudes, because the solubility of $CaCO_3$ increases with decreasing temperature and increasing pressure. Consequently, there is significant shoaling of the aragonite saturation horizons in the Pacific, north of ~40°N, at the equator, and 10°N, especially towards the east, because of the higher DIC concentrations relative to TA at shallower depths. These patterns result from enhanced upwelling that brings deeper waters rich in nutrients and DIC to the upper ocean (Figure 3) and supports high animal biomass. As one moves north, the aragonite saturation depth shoals from ~1000 m near 30°S to 300 m at the equator. Moving farther north, it deepens to 550 m near 30°N, then shoals to ~100 m north of 50°N (Figure 3). In the North Pacific, the upward migration of the aragonite saturation horizon from anthropogenic CO_2 uptake is currently ~1–2 m year^{-1} (Feely *et al.*, 2006).

Orr *et al.* (2005) developed model scenarios of future changes in surface ocean carbonate chemistry as a function of changes in atmospheric CO_2, using the IPCC IS92a "business-as-usual" CO_2 emission scenario, with the median projection of DIC changes from 13 ocean models that participated in the OCMIP-2 project. Based on their model outputs and global gridded data (Key *et al.*, 2004), we plotted the projected aragonite

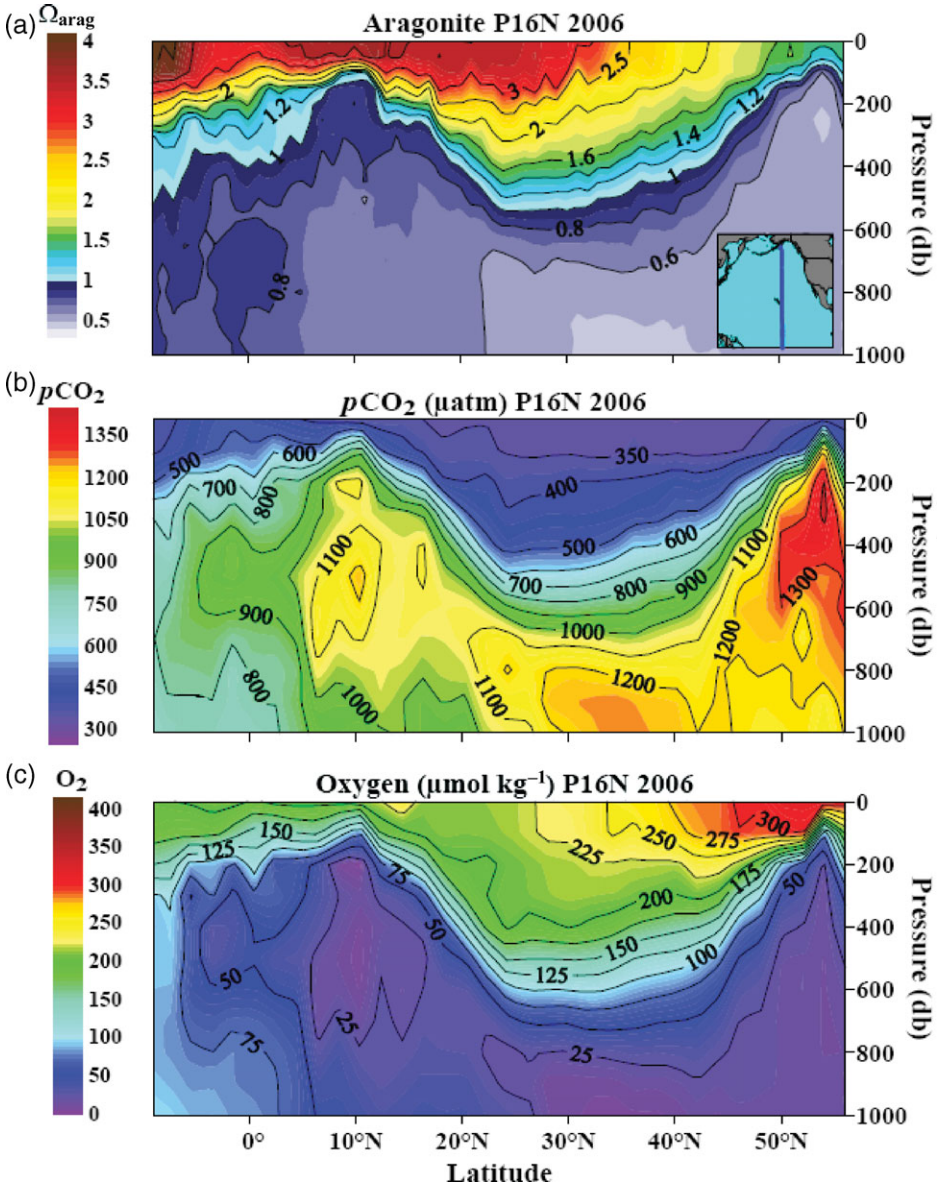

Figure 3. Distribution of (a) aragonite saturation; (b) partial pressure of CO_2 seawater (pCO_2); and (c) dissolved oxygen along the March 2006 P16 N transect along 152°W in the North Pacific.

saturation state of the surface oceans for the years 1765, 1994, 2050, and 2100 (Figure 4). The model results indicate that, by the time atmospheric CO_2 reaches 780 ppmv near the end of this century under the IPCC IS92a "business-as-usual" CO_2 emission scenario, portions of the Subarctic North Pacific and all of the Southern Ocean south of ~60°S will become undersaturated with respect to aragonite (Orr *et al.*, 2005). At that point, the global average surface water CO_3^{2-} concentration and aragonite and calcite saturation state will be nearly half of what they are today. The aragonite saturation horizons would also shoal from its present average depth of 730 m to the surface in the Southern Ocean, from 2600 to 115 m in the North Atlantic, and from 140 m to the surface in parts of the North Pacific (Orr *et al.*, 2005). In the cold, high-latitude surface waters typical of polar and subpolar regions of the Southern Ocean, aragonite and calcite undersaturation will occur when seawater pCO_2 values reach ~560 and 900 ppmv, respectively. In the slightly warmer surface waters of the subpolar North Pacific, aragonite and calcite undersaturation will occur later, when pCO_2 reaches 740 and 1040 ppmv, respectively. The cold waters of the Arctic Ocean are also naturally low in CO_3^{2-} concentration. Continuing research is evaluating how the Arctic Ocean's changes in carbonate chemistry during the 21st century will differ from those in the Southern Ocean (Orr *et al.*, 2006). The warm surface waters of the tropics and subtropics will not become undersaturated with respect to aragonite or calcite over the range of these projected conditions although, in some regions associated with upwelling, shoaling aragonite saturation horizons now impinge on the depth ranges of many pelagic animals (Feely *et al.*, 2004).

Priority areas for ocean acidification research are therefore high-latitude regions, which are projected to experience the greatest changes in carbonate chemistry over decadal to century

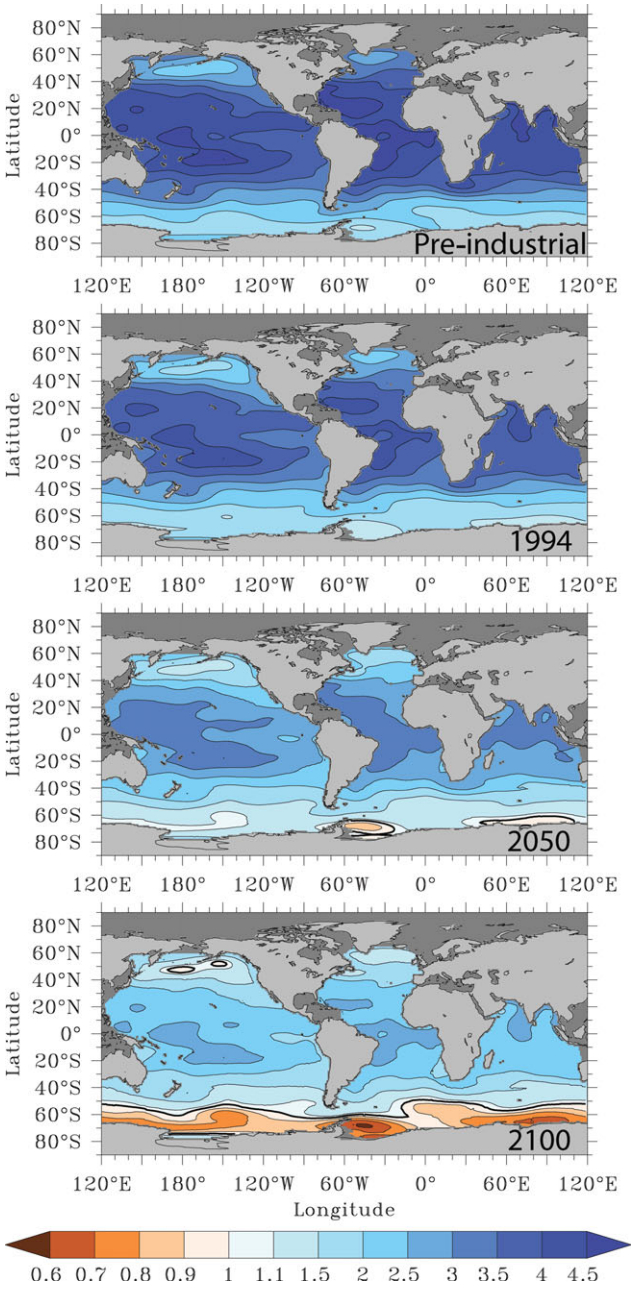

Figure 4. Surface water aragonite saturation state (Ω_{arag}) for the pre-industrial ocean (nominal year 1765), and years 1994, 2050, and 2100. Values for years 1765 and 1994 were computed from the global gridded data product GLODAP (Key *et al.*, 2004), whereas the saturation state for years 2050 and 2100 are the median of 13 ocean general circulation models forced under the IPCC's IS92a "business-as-usual" CO_2 emission scenario (Orr *et al.*, 2005).

time-scales. Moreover, coastal regions, which can be greatly impacted by anthropogenic-driven ocean acidification (Doney *et al.*, 2007), as well as eutrophication leading to low oxygen zones, are not well-represented in global ocean–atmosphere coupled models, because of lack of data, complexities of nearshore circulation processes, and too-coarse model resolution. Given the importance of coastal areas to fisheries and other marine resources and services, coastal ecosystems constitute another target region where research is urgently needed.

Effects of elevated pCO_2 on calcification

The secretion of $CaCO_3$ skeletal structures is widespread across animal phyla, and evolved independently and repeatedly over geologic time since the late Precambrian period (Knoll, 2003). Protection is one probable advantage of possessing a calcareous skeleton. Additionally, various other biotic and abiotic factors have probably contributed to selection for $CaCO_3$ hard parts in diverse groups of fauna at different times in evolutionary history.

Most calcifying organisms investigated to date demonstrate reduced calcification in response to increased pCO_2 and decreased $[CO_3^{2-}]$, $CaCO_3$ saturation state, and pH (e.g. Gattuso *et al.*, 1998; Langdon *et al.*, 2000, 2003; Riebesell *et al.*, 2000). The majority of work has tested warm-water corals and coccolithophorid algae (Royal Society, 2005; Kleypas *et al.*, 2006). Evidence suggests that the calcification rate in corals is controlled by the $CaCO_3$ saturation state (Gattuso *et al.*, 1998; Langdon *et al.*, 2000, 2003; Marubini *et al.*, 2001, 2003; Leclercq *et al.*, 2002; Ohde and Hossain, 2004; Langdon and Atkinson, 2005; Schneider and Erez, 2006; Silverman *et al.*, 2007), rather than pH or another parameter of the seawater CO_2 system. Because the $[Ca^{2+}]$ in the ocean today is approximately constant (depending predominantly on salinity), changes in the $[CO_3^{2-}]$ are reflected directly as changes in the $CaCO_3$ saturation state. In contrast, high $[Ca^{2+}]$ in the Cretaceous (Horita *et al.*, 2002) allowed planktonic calcifiers to flourish and large chalk deposits to accumulate (Bown *et al.*, 2004), despite CO_3^{2-} concentrations that were only ~25% of the current value (Tyrrell and Zeebe, 2004; Ridgwell and Zeebe, 2005). This observation supports the idea that the $CaCO_3$ saturation state [proportional to the product of Ca^{2+} and CO_3^{2-} concentrations as shown in Equation (1)] is the key component of the seawater carbonate system that controls calcification rates.

Holoplankton

The major planktonic $CaCO_3$ producers are the coccolithophores, foraminifera, and euthecosomatous pteropods. These three groups of calcifiers account for nearly all the export flux of $CaCO_3$ from the upper ocean to the deep sea. Planktonic foraminifera and coccolithophores secrete tests or shells made of calcite, whereas pteropods form shells made of aragonite, a metastable polymorph of $CaCO_3$, which is ~50% more soluble in seawater than calcite (Mucci, 1983). On a global basis, coccolithophores and foraminifera are thought to produce the majority of pelagic $CaCO_3$ (Schiebel, 2002), while the labile aragonitic shells of pteropods account for a smaller fraction of the total $CaCO_3$ produced by planktonic organisms. The relative contributions of these three groups of calcifiers can vary substantially on regional and temporal scales, however. There are few concurrent measurements of the abundances of all three groups, and estimates of their contributions to global calcification rates are poorly constrained.

Both planktonic foraminifera and euthecosomatous pteropods are widely distributed in the upper ocean, with highest species diversity in tropical and subtropical regions. Shelled pteropods can reach densities of 1000s to >10 000 of individuals m^{-3} in high-latitude areas (e.g. Bathmann *et al.*, 1991; Pane *et al.*, 2004) and are important components of polar and subpolar ecosystems. Data are limited on the response of calcification in pteropods and foraminifera to elevated pCO_2 and decreased $CaCO_3$ saturation state. Currently, evidence is available for only two of the ~50 species of planktonic foraminifera and only one of the ~34

euthecosome species. Although these data suggest that both groups reduce calcification in response to ocean acidification, the small number of species tested precludes the identification of general trends. Species-specific responses are likely, and it is possible that the calcification rates of some species may not be sensitive to elevated pCO_2, as has been found in coccolithophores (Riebesell *et al*., 2000; Langer *et al*., 2006).

In laboratory experiments with the symbiont-bearing planktonic foraminifera *Orbulina universa* and *Globigerinoides sacculifer*, shell mass decreased in response to reduced CO_3^{2-} concentration and calcite saturation state, even though the seawater was supersaturated with respect to calcite (Spero *et al*., 1997; Bijma *et al*., 1999, 2002). When grown in seawater chemistry equivalent to pCO_2 of 560 and 740 ppmv, shell mass in these species declined by 4–8 and 6–14%, respectively, compared with the pre-industrial pCO_2 value. Evidence from microelectrode and culture experiments suggests that elevated pH and CO_3^{2-} concentration in the micro-environment immediately adjacent to the shell are critical in promoting shell growth (Spero and Lea, 1993; Rink *et al*., 1998; Köhler-Rink and Kühl, 2005). When *O. universa* is grown under high light, the pH of the micro-environment surrounding the test can be increased up to 8.8 (0.5 units above ambient seawater) as a result of CO_2 removal during symbiont photosynthesis. In contrast, *O. universa* grown in the dark has a near-shell microenvironment pH of 7.9, owing to respiratory CO_2 release (Köhler-Rink and Kühl, 2005). Because of the large effect of symbiont photosynthesis on seawater CO_2 chemistry at the shell surface, it may be that the impact of ocean acidification on adult symbiont-bearing foraminifera will occur primarily during night calcification. It is unknown whether foraminifera that do not possess photosynthetic symbionts are more susceptible to reduced CO_3^{2-} concentration and calcite saturation state than those species with symbionts. Similarly, the post-zygote, prolocular ontogenetic stage of foraminifera, during which calcification is weak or absent and symbiotic algae have not yet been acquired (Brummer *et al*., 1987), may be particularly vulnerable to elevated pCO_2. Because it is currently impossible to maintain the prolocular stage in the laboratory, however, this hypothesis awaits testing.

A positive correlation between foraminiferal shell mass and ambient $[CO_3^{2-}]$ is observed in the sedimentary record as a response to known glacial–interglacial changes in atmospheric CO_2 of the past 50 000 years (Barker and Elderfield, 2002). However, Barker and Elderfield (2002) demonstrate an increase in *Globigerinoides bulloides* shell mass from 11 to 19 μg for a small change in $[CO_3^{2-}]$ from 210 to 250 μmol kg^{-1}, whereas Bijma *et al*. (2002) report a much greater increase, from 40 to 60 μg in shell mass for *O. universa* for a change in $[CO_3^{2-}]$ from 200 to 600 μmol kg^{-1}, and ~10 μg increase in shell mass for *G. sacculifer* for a change in $[CO_3^{2-}]$ from 100 to 600 μmol kg^{-1}. Although it appears that culture experiments may underestimate foraminiferal response to altered $[CO_3^{2-}]$ compared with the change observed in paleo-reconstructions over glacial-to-interglacial time-scales, temperature and food supply also strongly affect foraminiferal calcification (cf. Barker and Elderfield, 2002; Bijma *et al*., 2002). Hence, future increases in sea surface temperatures could lead to higher foraminiferal growth rates.

Owing to their highly soluble aragonitic shells, pteropods may be particularly sensitive to ocean acidification. When live *Clio pyramidata* collected in the Subarctic Pacific were exposed to a level of aragonite undersaturation similar to that projected for Southern Ocean surface waters in year 2100 under the IS92a emissions scenario, there was marked shell dissolution within 48 h (Feely *et al*., 2004; Orr *et al*., 2005). In additional experiments, *C. pyramidata* were placed in 1 l jars, and ^{45}Ca was added to measure shell calcification rates. The jars were then closed and incubated at 10°C for 4–48 h. At the start of this experiment, the seawater Ω_{arag} was ~2.4. Forty-eight hours later, respiratory CO_2 from the actively swimming pteropods had gradually forced the aragonite saturation state to drop below 1. The ^{45}Ca uptake experiments reveal progressively reduced calcification rates in concert with decreased aragonite saturation state that resulted from the accumulation of metabolic CO_2 produced by animals during the experiment (Figure 5). After 36–48 h, most of the ^{45}Ca that had been incorporated into shells had dissolved back into solution. Hence, by 36 h, net dissolution exceeded net calcification, although animals were alive and actively swimming. Scanning electron microscopic photographs of experimental shells confirm that dissolution occurred along the leading edge of the shell by 48 h during incubation in closed jars, but no dissolution was visible in control shells incubated in open jars, where the aragonite saturation remained >1 (Figure 6). Based on pteropod oxygen consumption rates (Smith and Teal, 1973), it is unlikely that animals were oxygen-stressed during these experiments, but future experiments should explore this possibility. Additional experiments are needed to measure calcification directly in euthecosomatous pteropods and foraminifera, as a function of $CaCO_3$ saturation state. It will also be necessary to study the interactive effects of $CaCO_3$ saturation state, temperature, and nutrition for multiple species and life stages of these calcareous holoplankton.

As pCO_2 rises and the $CaCO_3$ saturation state of surface ocean decreases, euthecosomatous pteropods and foraminifera may secrete under-calcified or thinner structures (Bijma *et al*., 1999). Should the habitat of these organisms approach $CaCO_3$ undersaturation, first with respect to aragonite, then with respect to calcite, the question of whether net rates of calcification can still exceed dissolution will likely depend on the degree of $CaCO_3$ undersaturation and the duration that animals are exposed to undersaturated waters. As yet, no decreases in calcification have been documented in field populations of either group. However,

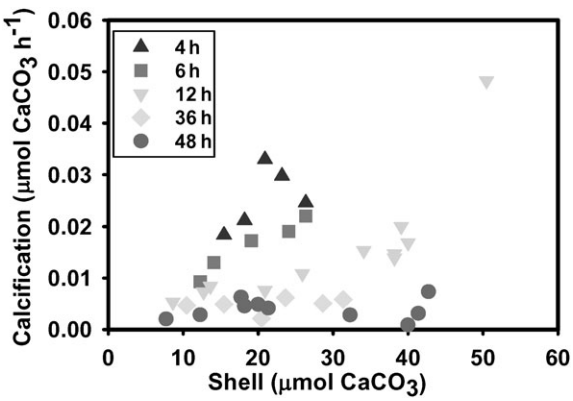

Figure 5. Net calcification (μmol $CaCO_3$ h^{-1}) as a function of shell $CaCO_3$ concentration for the Subarctic Pacific euthecosomatous pteropod *Clio pyramidata*. Different sizes of pteropods were incubated at 10°C in closed 1 l jars for 4–48 h. Net calcification rates decreased with time, as the aragonite saturation state of seawater was progressively reduced owing to respiratory CO_2 in sample containers.

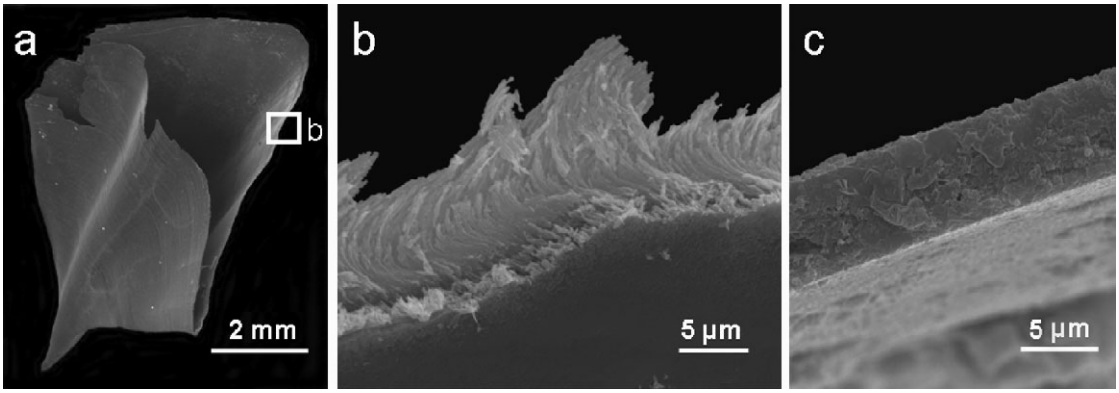

Figure 6. SEM photographs of the shell of the pteropod *Clio pyramidata*. (a) Whole shell of an animal incubated for 48 h in a closed container, wherein animal respiration forced the aragonite saturation state <1; (b) magnified portion of the leading edge of the shell section shown in (a), revealing dissolution of aragonitic rods; (c) magnified leading edge of the shell of a control animal incubated in seawater that remained supersaturated with aragonite for the duration of the experiment.

baseline data on their present-day vertical distributions and calcification rates are insufficient to detect possible changes that may result from ocean acidification.

The capacity of euthecosome and foraminifera species to adapt to progressively acidified ocean waters is not known, but may be related to species' generation time. If unabated CO_2 emissions continue and surface waters of the Southern Ocean and portions of the Subarctic Pacific become undersaturated with respect to aragonite by 2100 as projected (Orr *et al*., 2005), then shelled pteropods in these regions would have only ~50–150 generations to adapt to corrosive seawater, given that high-latitude pteropods are thought to have generation times of 0.6–1.5 years (Kobayashi, 1974; Bathmann *et al*., 1991; Dadon and de Cidre, 1992; Gannefors *et al*., 2005). Generation times for spinose species of foraminifera are frequently linked with the lunar cycle such that they reproduce every 2–4 weeks; however, non-spinose species probably have longer reproductive cycles (Hemleben *et al*., 1989). Shorter generation time affords increased opportunities for microevolutionary adaptation.

In addition to euthecosomes and foraminifera, other holoplankton calcify during part or all of their life cycles. These include the heteropods, visual predators that are found in the epipelagic zone of all tropical and subtropical oceans, but which are absent from high latitudes. Two of the three heteropod families possess aragonitic shells as adults, and species in the third family cast off their larval shells at metamorphosis. Gymnosomes, the highly specialized predators of euthecosomatous pteropods, possess a large veliger shell, presumed to be aragonite, which is also cast off at metamorphosis. Similarly, pseudothecosomatous pteropods possess a veliger shell that is discarded at metamorphosis to the gelatinous adult.

Benthic invertebrates

Nine multicellular invertebrate phyla have benthic representatives with $CaCO_3$ skeletal hard parts (Lowenstam and Weiner, 1989). These taxa secrete $CaCO_3$ in the form of aragonite, calcite, high-magnesium calcite (>5 mole % $MgCO_3$), amorphous $CaCO_3$, or a mixture of these $CaCO_3$ phases. Amorphous $CaCO_3$ is less stable than the crystalline phases of $CaCO_3$, and the seawater solubility of high-magnesium calcite is similar to or greater than that of aragonite (Walter and Morse, 1985; Bischoff *et al*., 1987). Many benthic calcifying fauna are prominent in nearshore communities and are economically and/or ecologically important. For example, bivalves, such as mussels and oysters, have high commercial value as fisheries and are also important as ecosystem engineers in coastal areas, providing habitat and other services for a rich diversity of organisms (Gutiérrez *et al*., 2003). Recent work suggests that benthic adult molluscs and echinoderms are sensitive to changes in seawater carbonate chemistry. In response to an elevated pCO_2 level projected to occur under the IS92a emissions scenario (~740 ppmv in 2100), calcification rates in the mussel *Mytilus edulis* and the Pacific oyster *Crassostrea gigas* decreased by 25 and 10%, respectively (Gazeau *et al*., 2007). When grown for more than six months in seawater bubbled with air containing 560 ppmv CO_2, a decrease in shell growth was observed in the edible snail *Strombus luhuanus*, and a reduction in wet weight was reported in both this snail and two species of sea urchins (Shirayama and Thorton, 2005).

Early calcifying stages of benthic molluscs and echinoids demonstrate a strong response to increased seawater pCO_2 and decreased pH, CO_3^{2-} concentration, and $CaCO_3$ saturation state. In the sea urchins *Hemicentrotus pulcherrimum* and *Echinodetra mathaei*, fertilization success, developmental rates, and larval size all decreased with increasing CO_2 concentration (Kurihara and Shirayama, 2004). Abnormal skeletalgenesis of the highly soluble high-magnesium $CaCO_3$ spicules in urchin larvae was also observed. Green *et al*. (2004) found that newly settled juveniles of the hard-shell clam *Mercenaria mercenaria* revealed substantial shell dissolution and increased mortality when they were introduced to surface sediments that were undersaturated with respect to aragonite (Ω_{arag} ~0.3), a level that is typical of nearshore, organic-rich surficial sediments. Within two weeks of settlement, the $CaCO_3$ shells were completely dissolved, leaving only the organic matrix of the shell.

The mineralogy and calcification mechanisms of mollusc and echinoid larval stages may render them particularly sensitive to ocean acidification. Although adult gastropods and bivalves secrete aragonite, calcite, or both phases in a diverse array of structural patterns, Weiss *et al*. (2002) suggest that veliger shells of gastropods and bivalves all contain aragonite in similar crystalline ultrastructures, and hence, the mollusc larval shell is highly conserved in evolution. Moreover, recent work using infrared

spectrometry and Raman imaging spectroscopy reveals that larvae of the clam *M. mercenaria* (adult shell is aragonitic), as well as that of the oyster *C. gigas* (adult shell is nearly entirely calcitic), form amorphous $CaCO_3$ as a transient precursor to aragonite (Weiss *et al.*, 2002). Similarly, during the embryonic development of two species of sea urchins, an amorphous $CaCO_3$ precursor transforms to calcite during spicule formation (Beniash *et al.*, 1997; Raz *et al.*, 2003). Because this unstable, transient, amorphous $CaCO_3$ is more soluble than the crystalline minerals of aragonite or calcite, biomineralization processes that occur during the embryonic and larval development of sea urchins, and in gastropod and bivalve molluscs, may be particularly vulnerable to ocean acidification.

$CaCO_3$ skeletal elements are also present in species of other benthic invertebrates, such as crustaceans, cnidarians, sponges, bryozoans, annelids, brachiopods, and tunicates. Apart from warm-water corals, nothing is known about the effect of elevated ambient pCO_2 on calcification rates in these taxa. Some of these animals may use shell dissolution to support acid-based regulation at high internal pCO_2, as has been observed in mussels (Michaelidis *et al.*, 2005) and other organisms.

Other non-skeletal, calcified secretions of marine fauna

In addition to using $CaCO_3$ for strengthening skeletal structures, the use of calcium minerals in gravity sensory organs is widespread among ocean fauna. In the many zooplankton and benthic invertebrates that possess statoliths, statocysts, or statocontia, the mineralogy is indeterminate or is reported to be amorphous Ca–Mg–phosphate or gypsum (Lowenstam and Weiner, 1989). In squid and fish, however, the statoliths and otoliths are composed of aragonite. Gravity sensory organs can have additional functions in some organisms. For example, in planktonic gymnosome snails, statocysts also are actively involved in the motor neural programme that underlies search movements for prey during hunting behaviour (Levi *et al.*, 2004). Whether mineralization of the various types of gravity receptors would be affected by the changing carbonate chemistry of seawater and, if so, how that might impact overall fitness of the organism, are questions that have not been investigated. Presumably, potential impacts would depend on the ability of the organisms to regulate the acid–base balance in the tissues surrounding those structures.

Other carbonate secretions of marine fauna include gastroliths, mineralized structures formed in the lining of the cardiac stomachs of some decapods that serve as storage sites for calcium during moult intervals; gastroliths can be calcite, amorphous $CaCO_3$, or calcium phosphate (cf. Lowenstam and Weiner, 1989). Widespread among marine fish is the intestinal secretion of calcium- and magnesium-rich carbonate complexes, which are then excreted via the rectum; this process appears to play a critical role in osmoregulation (Walsh *et al.*, 1991; Grosell, 2006; Taylor and Grosell, 2006).

Consequences of reduced calcification

The effects of chronic exposure to increased CO_2 on calcifiers, as well as the long-term implications of reduced calcification rates within individual species and their ecological communities, are unknown. Calcification probably serves multiple functions in carbonate producers. Decreased calcification would presumably compromise the fitness of these organisms and could shift the competitive advantage towards non-calcifiers. Such a consequence is supported by recent work with warm-water reef organisms in which a decreased aragonite saturation state induced the transition from a $CaCO_3$-dominated system to one dominated by organic algae (Kuffner *et al.*, 2008).

Increased pCO_2 and other physiological processes

In addition to calcification, a number of other physiological indices appear to correlate with the capacity for acid–base tolerance, and new data are emerging that test the survival, growth, development, metabolism, and pH balance of organisms under elevated pCO_2. Prior to 1995, most studies used CO_2 values that were well above what is expected in the future ocean and from convenient marine animal models, in order to reveal the fundamental mechanisms associated with acid–base regulation. Studies conducted more recently have tested the physiological response to very high CO_2 levels as would be associated with purposeful sequestration of CO_2 in the ocean. There is now a critical need to test the physiological consequences of ocean acidification at lower pCO_2 levels, such as those that are projected to occur over the next century.

Mechanisms to deal with hypercapnia

When pCO_2 levels increase in seawater, dissolved CO_2 more readily diffuses across animal surfaces and equilibrates in both intra- and extracellular spaces. Internal levels rise until a new value is reached that is sufficient to restore CO_2 excretion against the elevated environmental level. As in seawater, CO_2 reacts with internal body fluids causing H^+ to increase and, therefore, pH to decrease. Mechanisms available to counteract this acidification are limited and relatively conserved across animal phyla. The mechanisms are the same as those evolved to deal with metabolically produced CO_2 and hydrogen ions. They include (i) passive buffering of intra- and extracellular fluids; (ii) transport and exchange of relevant ions; (iii) transport of CO_2 in the blood in those species that have respiratory pigments; (iv) metabolic suppression to wait out periods of elevated CO_2 (e.g. Somero, 1985; Truchot, 1987; Cameron, 1989; Walsh and Milligan, 1989; Hand, 1991; Heisler, 1993; Guppy and Withers, 1999; Clairborne *et al.*, 2002; Seibel and Walsh, 2003; Pörtner *et al.*, 2004). Those species adapted to environments with steep CO_2 gradients, such as hydrothermal vents or stagnant tide pools, and those species with high capacity for metabolic production of CO_2 have evolved greater capacities for buffering, ion exchange, and CO_2 transport (Seibel and Walsh, 2001, 2003). Whether such elevated capacity translates into greater tolerance of chronic ocean acidification remains to be seen.

Buffering capacity

When concentrations are elevated, CO_2 readily crosses biological membranes and enters the blood and intracellular spaces. Passive buffering is the only mechanism immediately available to limit pH changes within the body. Locomotory muscles of active animals, such as epipelagic fish and cephalopods, have high activities of anaerobic metabolic enzymes and, consequently, have high capacity for buffering pH changes associated with anaerobically fuelled burst locomotion (Castellini and Somero, 1981; Seibel *et al.*, 1997). Organisms with low buffering capacity will experience greater fluctuations in intracellular pH during hypercapnia than others with higher capacity. For example, an increase in seawater pCO_2 sufficient to lower intracellular pH by 0.2 in a sluggish benthic fish may cause only a 0.02 pH unit drop in an active

epipelagic fish such as tuna (Seibel and Walsh, 2003). Buffering of extracellular fluid is, in some cases, also provided by formation of bicarbonate from dissolution of $CaCO_3$ stores or exoskeletons (shells or tests) as discussed below.

Ion transport

In the longer term (hours to days), compensation of acid–base imbalance relies on the ability to transport acid–base equivalent ions across cell membranes. The CO_2 that is produced in the cells during routine metabolism is typically hydrated to form bicarbonate and H^+, a reaction catalyzed by the enzyme carbonic anhydrase. These hydrogen ions are then buffered in the intracellular space as discussed above, while the bicarbonate is transported out of the cell in exchange for Cl^- via ion transport proteins. Species with ineffective ion transport capacities are poorly equipped for acid–base regulation (Heisler, 1989; Walsh and Milligan, 1989). Low rates of metabolism typically correlate with lower concentrations of ion transport proteins such as Na^+/K^+ and H^+-ATPases (Gibbs and Somero, 1990), suggesting reduced capacities of acid–base balance. In many cases, the gelatinous tissues (e.g. mesoglea) found in diverse zooplankton are distinct from the muscle tissues that are most metabolically active (Thuesen *et al.*, 2005a, b). Therefore, the active tissues of gelatinous animals may have greater CO_2 tolerance than would be estimated, based on rates of whole-animal metabolism. Similarly, species not exposed to environmental fluctuations in CO_2 may also be ill-equipped to handle ocean acidification. For example, species from hydrothermal vents have high activities of carbonic anhydrase relative to species from shallower environments. Even lower still are carbonic anhydrase activities of benthic deep-sea species, far removed from venting water, that experience very little fluctuation in environmental CO_2 (Figure 7). Compensation of acidosis via adjustments in ionic composition appears to be a trade-off that is not likely sustainable on longer time-scales, such as that associated with anthropogenic increases in seawater pCO_2. Nevertheless, a survey of species that are more or less able to regulate the pH of their internal fluids may be informative.

Acid–base regulation via bicarbonate accumulation

A common component of pH compensation in animals is the intracellular accumulation of HCO_3^- (Walsh and Milligan, 1989; Pörtner and Reipschläger, 1996) that drives an elevation in pH. A "bicarbonate threshold" is hypothesized (Heisler, 1993; Pörtner and Reipschläger, 1996), above which the capacity for further compensation is limited. Although additional bicarbonate accumulation will always further compensate reduced pH, there may be an upper limit beyond which acid–base regulation begins to compromise ionic balance (Cameron and Iwama, 1987). Those species that can tolerate accumulation of bicarbonate to levels 4–10 times above control conditions appear generally more tolerant of hypercapnia, whereas those with limited bicarbonate accumulation may be more vulnerable.

Miles *et al.* (2007) recently found incomplete compensation of coelomic fluid pH, despite elevated bicarbonate levels under all CO_2 exposures (pH 6.2–7.4), in an intertidal sea urchin. Dissolution of the high magnesium calcite test was inferred from elevations in coelomic Mg^{2+}, and the authors suggested that reductions in surface seawater pH below 7.5 would be severely detrimental to this species, and probably other sea urchins as well. These results are consistent with those of Burnett *et al.* (2002) and Spicer (1995), demonstrating that sea urchins are unable to compensate acidosis resulting from short-term emersion and hypoxia, respectively.

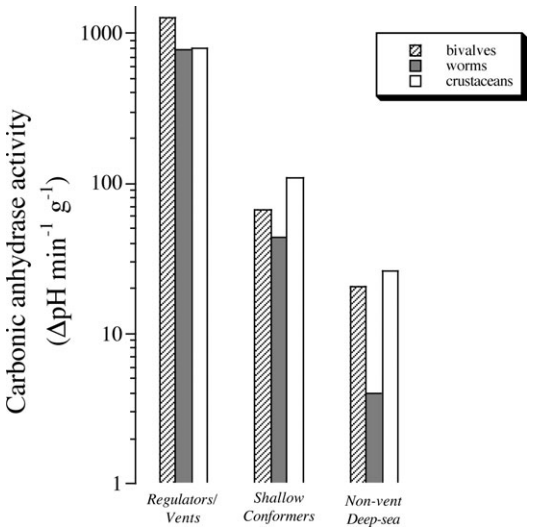

Figure 7. Carbonic anhydrase activity (ΔpH min g wet mass^{-1}) in gas exchange tissue of benthic macrofauna in habitats with large fluctuations in environmental pCO_2. Bivalves (hatched bars), worms (grey bars), and crustaceans (open bars). Each bar represents the mean of several species (note the *x*-axis is on a log scale). Species are grouped as ionic regulators (euryhaline species including those from hydrothermal vents), shallow-living ionic conformers (those from stable shallow-water habitats), and deep-sea conformers. Data for worms and bivalves are from Kochevar and Childress (1996). Data for crustaceans are from Henry (1984) and unpublished observations (J. Company, pers. comm.).

Similarly, the mussel *M. edulis* compensated both short- and long-term exposure to 1% CO_2 (~10 000 ppmv) by dissolution of its shell as indicated by increased Ca^+ levels (Lindinger *et al.*, 1984; Michaelidis *et al.*, 2005). Not surprisingly, long-term exposure resulted in reduced growth and metabolism. A deep-sea crab measured recently by Pane and Barry (2007) failed to accumulate any bicarbonate or control haemolymph pH values over 24 h exposure to hypercapnia. This poor performance was attributed to low rates of metabolism, stable environmental conditions, and reduced oxygen at depth that may have limited ion exchange capacity. In short-term experiments, the sipunculid worm *Sipunculus nudus* demonstrated hypercapnic tolerance, with only a 50% elevation in extracellular bicarbonate relative to control levels (Pörtner and Reipschläger, 1996). The reduced metabolic rate observed in this species (40% of control values), under natural, short-term elevation of CO_2, allows survival until well-aerated waters return with high tide. However, over the longer term (3–6 week), such metabolic suppression resulted in 100% mortality (Langenbuch and Pörtner, 2004).

Species that are more tolerant exhibit greater bicarbonate accumulation and, consequently, compensate more completely the acidosis caused by exposure to elevated CO_2. For example, exposure of the subtidal crab *Necora puber* to pCO_2 ~10 000 ppmv resulted in haemolymph bicarbonate concentrations more than four times the control levels, in part supplied by shell dissolution (Spicer *et al.*, 2007). Similarly, the crab *Cancer magister* fully compensated its haemolymph pH over

24 h by accumulating more than 12 mM bicarbonate (Pane and Barry, 2007). Fish appear most tolerant among marine animals. The Mediterranean fish *Sparus aurata* was able to compensate completely both blood plasma pH and intracellular pH in the face of 10 000 ppm pCO_2 via elevations in bicarbonate to five times the control levels. No mortality occurred after ten days of exposure (Michaelidis *et al*., 2007). Although feed intake was reduced at a seawater pH of 7.25, compensation of internal acid–base imbalance was accomplished in the sea bass *Dicentrarchus labrax* via a fivefold elevation in plasma bicarbonate (Cecchini *et al*., 2001).

Mortality

Mortality occurred in three fish species tested, including yellowtail and flounder, only at very high CO_2 levels (>50 000 ppmv) after 24 h exposure, and the authors concluded that fish mortality caused by anthropogenic CO_2 is never expected in marine environments (Hayashi *et al*., 2004). Although we believe that this statement is premature, marine fish do appear highly tolerant of CO_2 (Kikkawa *et al*., 2004, 2006). The hatchling stages of some species appeared fairly sensitive to pH decreases on the order of 0.5 or greater, but high CO_2 tolerance developed within a few days of hatching (Ishimatsu *et al*., 2004). The relative tolerance of fish and others may relate to high capacity for internal ion and acid–base regulation via direct proton excretion (Ishimatsu *et al*., 2004) and an intracellular respiratory protein that results in a high oxygen-carrying capacity and substantial venous oxygen reserve. When compensation of pH fails, mortality of all marine animals increases with the level of CO_2 and the duration of exposure (Yamada and Ikeda, 1999; Hayashi *et al*., 2004; Watanabe *et al*., 2006; Table 1).

Metabolic suppression

If compensation of acid–base imbalance is not achieved, reduced pH and elevated pCO_2 may depress metabolism in some species (Hand, 1991; Pörtner and Reipschläger, 1996; Guppy and Withers, 1999; Figure 8). Metabolic suppression is considered an adaptive strategy for the survival of short-term hypercapnia and hypoxia. During periods of environmental oxygen limitation, many organisms are able to suppress ATP demand, thereby extending the duration of tolerance. In many cases, oxygen limitation is coincident with internal acid–base disturbance. Metabolic suppression is not advantageous, however, under chronic elevations of CO_2 (e.g. *S. nudus*, as cited above; Langenbuch and Pörtner, 2004). Metabolic suppression is typically achieved by shutting down expensive processes. Chief among these is protein synthesis (Hand, 1991). Reduced protein synthesis, by definition, will reduce growth and reproductive potential. Although suppression of metabolism under short-term experimental conditions is a "sublethal" reversible process, reductions in growth and reproductive output will effectively diminish the survival of the species on longer time-scales.

Blood-oxygen binding

Many marine animals rely on specialized respiratory proteins to bind oxygen at respiratory surfaces (e.g. gills) and deliver it to the tissues for cellular metabolism. A high gradient from the environment to the blood promotes oxygen binding at the gills, and the gradient from the blood to the metabolizing tissues promotes its release. However, these gradients alone are often inadequate to facilitate sufficient oxygen saturation and unloading of the respiratory proteins. CO_2 produced by cellular metabolism interacts with body fluids to produce hydrogen ions that bind to respiratory proteins, altering their affinity for oxygen. That is, CO_2 production causes acidosis that promotes oxygen release at the tissues, whereas CO_2 excretion elevates pH and promotes oxygen binding at the gills. The sensitivity of oxygen binding to pH is expressed as the Bohr coefficient ($\Delta \log P_{50}/\Delta pH$, where P_{50} is the pO_2 required to achieve 50% oxygen saturation of the respiratory protein). The biotic and abiotic factors that contribute to selective pressure for pH sensitivity are complex and not easily predicted, and the measurement of pH sensitivity and blood oxygen binding depends on various ionic and organic modulators that vary tremendously from one study to another (Lallier and Truchot, 1989; Mangum, 1991). All else being equal, however, greater pH sensitivity (a larger Bohr effect) may allow more complete release of oxygen in support of high oxygen demand, or from high-affinity respiratory proteins, such as those of species adapted to hypoxic environments (Childress and Seibel, 1998; Hourdez and Weber, 2005).

Pörtner and Reipschläger (1996) predicted that species with high metabolic rates would be more severely impacted by ocean acidification because oxygen binding in their blood is more pH sensitive. Epipelagic squid (e.g. Ommastrephidae, Gonatidae, Loliginidae) are hypothesized to be most severely impacted by the interference of CO_2 with oxygen binding at the gills, because their metabolic rates are higher than other aquatic animals (Seibel, 2007; Seibel and Drazen, 2007). Furthermore, oxygen carrying capacity is constrained in squid relative to active fish (Pörtner, 1994). As a result, it is necessary for active squid to utilize all of the oxygen carried in the blood on each pass through the body, even at rest, leaving no venous oxygen reserve. Unloading the entire oxygen store at the tissues requires extreme pH sensitivity (Bohr coefficient less than −1.0; Figure 9; Pörtner, 1994). One downside of this adaptation is that an increase in CO_2 in the environment will inhibit oxygen binding at the gills. Pörtner (1990, 1994) estimates that a reduction in environmental seawater pH by as little as 0.15 unit will reduce the scope for activity in the squid *Illex illecebrosus*. Recent work demonstrates that elevated pCO_2 (~1000 ppmv) can create measurable reductions in the oxygen consumption rate and scope for activity of another ommastrephid squid *Dosidicus gigas* (Figure 8; R. Rosa and B. Seibel, unpublished data). However, squid may be exceptional both metabolically and in their sensitivity to low pH. We review the pH sensitivity of oxygen binding in marine animals and find no correlation with metabolic rate or environmental oxygen levels and find no obvious phylogenetic signal (Figure 9). For example, several metabolically active species have pH insensitive respiratory proteins (low Bohr coefficients), while several others have high pH sensitivity despite low oxygen demand.

Predicting population and ecosystem responses

Table 1 lists the responses of a variety of animals to low pH–high pCO_2 conditions. The data indicate that foraminifera, molluscs, and echinoderms demonstrate reduced calcification and sometimes dissolution of $CaCO_3$ skeletal structures when exposed to elevated pCO_2 and decreasing pH and CO_3^{2-} concentration. Fertilization rates and early development are also negatively impacted by high CO_2 conditions in a number of groups such as sea urchins, molluscs, and copepods. Significantly, the data are limited with regard to the number of species tested at climate-relevant pCO_2 levels. For example, although teleost fish

Table 1. Examples of the response of marine fauna to ocean acidification.

Species	Description	CO_2 system parameters	Sensitivity	Reference
Planktonic foraminifera				
Orbulina universa	Symbiont-bearing	pCO_2 560–780 ppmv	8–14% reduction in shell mass	Spero *et al.* (1997); Bijma *et al.* (1999, 2002)
Globigerinoides sacculifer	Symbiont-bearing	pCO_2 560–780 ppmv	4–8% reduction in shell mass	Bijma *et al.* (1999, 2002)
Cnidaria				
Scyphozoa Hydrozoa	Jellyfish	North Sea seawater pH drop from 8.3 to 8.1	Increase in frequency as measured by CPR from 1958 to 2000	Attrill *et al.* (2007)
Mollusca				
Clio pyramidata	Shelled pteropod	$\Omega_{arag} < 1$	Shell dissolution	Feely *et al.* (2004); Orr *et al.* (2005); this work
Haliotis laevigata	Greenlip abalone	pH 7.78; pH 7.39	5% and 50% growth reductions	Harris *et al.* (1999).
Haliotis rubra	Blacklip abalone	pH 7.93; pH 7.37	5% and 50% growth reductions	
Mytilus edulis	Mussel	pH 7.1 / 10 000 ppmv	Shell dissolution	Lindinger *et al.* (1984)
		pCO_2 740 ppmv	25% decrease in calcification rate	Gazeau *et al.* (2007)
Crassostrea gigas	Oyster	pCO_2 740 ppmv	10% decrease in calcification rate	
Mytilus galloprovincialis	Mediterranean mussel	pH 7.3, ~5000 ppmv	Reduced metabolism, growth rate	Michaelidis *et al.* (2005)
Placopecten magellanicus	Giant scallop	pH < 8.0	Decrease in fertilization and embryo development	Desrosiers *et al.* (1996)
Tivela stultorum	Pismo clam	pH <8.5	Decrease in fertilization rates	Alvarado-Alvarez *et al.* (1996)
Pinctada fucada martensii	Japanese pearl oyster	pH 7.7	Shell dissolution, reduced growth	Reviewed in Knutzen (1981)
		pH >7.4	Increasing mortality	
Mercenaria mercenaria	Clam	$\Omega_{arag} = 0.3$	Juvenile shell dissolution leading to increased mortality	Green *et al.* (2004)
Illex illecebrosus	Epipelagic squid	2000 ppmv	Impaired oxygen transport	Pörtner and Reipschläger (1996)
Dosidicus gigas	Epipelagic squid	0.1% CO_2, ~1000 ppmv	Reduced metabolism/scope for activity	Rosa and Seibel (unpublished)
Arthropoda				
Acartia steueri	Copepod	0.2-1%CO_2,	Decrease in egg hatching success;	Kurihara *et al.* (2004)
Acartia erythraea	Copepod	~2000–10 000 ppmv	increase in nauplius mortality rate	
Copepods	Pacific, deep vs. shallow	860–22 000 ppmv CO_2	Increasing mortality with increasing CO_2 concentration and duration of exposure	Watanabe *et al.* (2006)
Euphausia pacifica	Krill	pH < 7.6	Mortality increased with increasing exposure time and decreasing pH	Yamada and Ikeda (1999)
Paraeuchaeta elongata	Mesopelagic copepod			
Conchoecia sp.	Ostracod			
Cancer pagurus	Crab	1% CO_2, ~10 000 ppmv	Reduced thermal tolerance, aerobic scope	Metzger *et al.* (2007)
Chaetognatha				
Sagitta elegans	Chaetognath	pH <7.6	Mortality increased with increasing exposure time and decreasing pH	Yamada and Ikeda (1999)
Echinodermata				
Strongylocentrotus purpuratus	Sea urchin	pH ~6.2–7.3	High sensitivity inferred from lack of pH regulation and passive	cf. Burnett *et al.* (2002)
Psammechinus miliaris	Sea urchin		buffering via test dissolution during emersion	Spicer (1995); Miles *et al.* (2007)
Hemicentrotus pulcherrimus	Sea urchin	~500–10 000 ppmv	Decreased fertilization rates, impacts larval development	Kurihara and Shirayama (2004)
Echinometra mathaei	Sea urchin			
Cystechinus sp.	Deep-sea urchin	pH 7.8	80% mortality under simulated CO_2 sequestration	Barry *et al.* (2002)

Continued

Table 1. *Continued*

Species	Description	CO_2 system parameters	Sensitivity	Reference
Sipuncula				
Sipunculus nudus	Peanut worm	1% CO_2, 10 000 ppmv	Metabolic suppression	Pörtner and Reipschläger (1996)
			Pronounced mortality in 7-week exposure	Langenbuch and Pörtner (2004)
Vertebrata				
Scyliorhinus canicula	Dogfish	pH 7.7 / 0.13%CO_2	Increased ventilation	Reviewed in Truchot (1987)
		7% CO_2, ~70 000 ppmv	100% mortality after 72 h	Hayashi *et al.* (2004)
Sillago japonica	Japanese whiting	7% CO_2, ~70 000 ppmv	Rapid mortality in 1-step exposure	Kikkawa *et al.* (2006)
Paralichthys olivaceus	Japanese flounder	5% CO_2, ~50 000 ppmv	100% mortality within 48 h	Hayashi *et al.* (2004)
Euthynnus affinis	Eastern little tuna	15%CO_2, ~150 000 ppmv	100% mortality of eggs after 24 h	Kikkawa *et al.* (2003)
Pagrus major	Red sea bream	5%CO_2, ~50 000 ppmv	>60% larval mortality after 24 h	Ishimatsu *et al.* (2005)
Seriola quinqueradiata	Yellowtail/ amberjack	5% CO_2, 50 000 ppmv	Reduced cardiac output; 100% mortality after 8 h	Ishimatsu *et al.* (2004)
Sparus aurata	Mediterranean fish	pH 7.3, ~ 5000 ppmv	Reduced metabolic capacity	Michaelidis *et al.* (2007)
Dicentrarchus labrax	Sea bass	pH 7.25, 24 mg l^{-1} CO_2	Reduced feed intake	Cecchini *et al.* (2001)

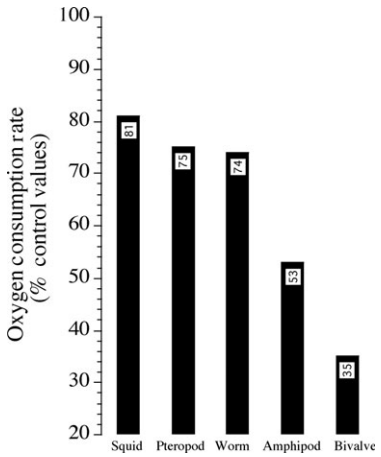

Figure 8. Oxygen consumption rates under elevated CO_2 for marine animals as a percentage of control rates (air saturation). Decreases in routine metabolism, an adaptive strategy to short-term hypercapnia, of the squid *Dosidicus gigas* ~1000 ppmv (0.1% at 20°C), the pteropod mollusc *Limacina helicina antarctica* under 789 ppmv (−1.86°C), the worm *Sipunculus nudus* and an amphipod *Phronima sedentaris* under 10 000 ppm (1.0%), and the bivalve *Mytilus edulis* under ~5000 ppmv (0.5%, pH 7.3, 18°C) carbon dioxide. (R. Rosa, and B. Seibel, unpublished data; Pörtner and Reipschläger (1996); Michaelidis *et al.* (2005)).

may appear less sensitive to decreased pH-elevated pCO_2 compared with other faunal groups, it must be emphasized that there is no information on the response of fish to the pCO_2 values that are projected to occur over the next century. Moreover, most empirical evidence comes from short-term experiments, and we know little or nothing about the response of marine biota to continuous, long-term exposure to elevated pCO_2 or the capacity of these organisms to adapt. Nevertheless, the data in Table 1 clearly demonstrate that elevated pCO_2 can adversely impact marine fauna both via decreased carbonate saturation state, which directly affects calcification rates, and via disturbance to acid–base physiology. We use the available evidence to speculate on possible ecological winners and losers during the 21st century, and to identify priorities for critically needed research.

Species distributions

Euthecosomatous pteropods will be first among the major groups of planktonic calcifiers to experience persistent <1 saturation states in surface waters of their current geographical ranges (Figures 3 and 4). If we assume that these animals are restricted to aragonite-saturated waters, then euthecosomatous pteropod habitat would become increasingly limited, first vertically in the water column, then latitudinally, by shoaling of the aragonite saturation horizon (Orr *et al.*, 2005). For example, the pteropod *C. pyramidata* is widely distributed and, in the North Pacific, its range extends to nearly 55°N. In other oceans, this species is typically found at 400–500 m during the day and in surface waters at night (Bé and Gilmer, 1977). If *C. pyramidata* has a similar pattern of vertical migration in the North Pacific, then this species would already be experiencing seawater corrosive to aragonite ($\Omega < 1$) during part of its diel cycle at ~10°N and near 50°N (Figure 3). When *C. pyramidata* is transported from coastal waters via anticyclonic Haida eddies that form along the eastern margin of the Subarctic Pacific and move towards the Alaskan gyre, this pteropod can be a dominant member of the eddy zooplankton community (Mackas and Galbraith, 2002; Tsurumi *et al.*, 2005). Yet, *C. pyramidata* demonstrated only weak diel vertical migration within an eddy, with most individuals remaining in the upper

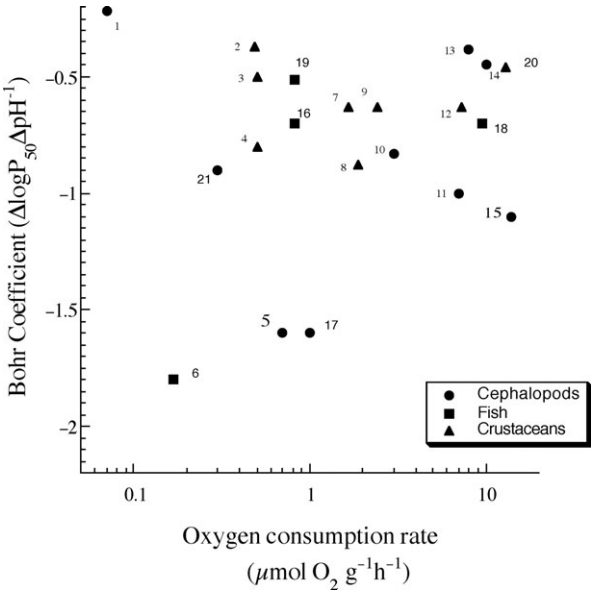

Figure 9. Bohr coefficients ($\Delta\log P_{50}\Delta pH^{-1}$), an indication of the sensitivity of oxygen transport to pH, as a function of oxygen consumption rate at approximate environmental temperature for marine animals from both benthic and pelagic environments. 1. *Vampyroteuthis infernalis*; 2. *Glyphocrangon vicara*; 3. *Bythograea thermydron*; 4. *Gnathophausia ingens*; 5. *Octopus vulgaris*; 6. *Coryphanoides armatus*; 7. *Acanthephyra curtirostris*; 8. *Acanthephyra acutifrons*; 9. *Systelaspis debilis*; 10. *Architeuthis* sp., 11. *Loligo pealei*; 12. *Acanthephyra smithi*; 13. *Loligo vulgaris*; 14. *Oplophorus gracilirostris*; 15. *Illex illecebrosus*; 16. *Sepia officinalis*; 17. *Octopus dofleini*; 18. *Trematomus bernacchii*; 19. *Artedidraco* sp.; 20. *Lolliguncula brevis*; 21. *Megaleledone senoi*. Bohr coefficients from Grigg (1967); Arp and Childress (1985); Noble *et al.* (1986); Sanders and Childress (1990); Eastman (1993); Bridges (1994); Tamburrini *et al.* (1998); Seibel *et al.* (1999); Lowe *et al.* (2000); Zielinski *et al.* (2001). Metabolic rates reviewed in Childress (1995); Seibel and Drazen (2007)). Metabolic rate for *Architeuthis* sp. is estimated from activity of citrate synthase.

75 m during both day and night (Mackas and Galbraith, 2002). Apart from this Haida eddy study, however, data on the vertical distribution of *C. pyramidata* in the Subarctic Pacific are lacking.

The euthecosome *Limacina helicina* is an important high-latitude species in both the northern and southern hemispheres. In the Arctic Ocean, this species is most abundant between 50–100 m during winter and in the upper 50 m during summer (Kobayashi, 1974). South of the Antarctic Polar Front, where aragonite undersaturation of the entire water column is projected to occur within the next 50–100 years, this pteropod species comprises nearly all of the of $CaCO_3$ export to the ocean interior (Collier *et al.*, 2000; Honjo *et al.*, 2000; Accornero *et al.*, 2003).

As aragonite saturation states approach 1 with progressive acidification during the 21st century (Figure 4), we hypothesize that shelled pteropod species, such as *C. pyramidata* and *L. helicina*, either will have to adapt to living continuously in seawater undersaturated with respect to aragonite or restrict their vertical and latitudinal distributions to warmer, more carbonate-rich regions that remain supersaturated with respect to aragonite. This latter possibility may be limited by the extreme adaptations to low temperature that may prevent equatorward movement of polar animals (Stillman, 2003; Somero, 2005; Seibel *et al.*, 2007). Waters undersaturated with respect to aragonite are currently impinging upon the depth ranges of pteropods in several other regions, such as upwelling areas associated with the Benguela Current, western Arabian Sea, and Peru Current, where pteropod abundances can be high (e.g. Bé and Gilmer, 1977; Fabry, 1990; Boltovskoy *et al.*, 1993; Kalberer *et al.*, 1993; Hitchcock *et al.*, 2002; Mohan *et al.*, 2006).

Although future anthropogenically induced reductions in the saturation state of calcite will not be as severe as those for aragonite, species of the calcitic foraminifera may also change their geographic distributions in response to decreased calcite saturation states. As calcite undersaturation is projected to occur ~50–100 years subsequent to that of aragonite (Orr *et al.*, 2005), foraminifera could be displaced from high latitudes, where they can be abundant. Changes in species composition could also occur, as has been reported in the California Current in response to anthropogenic warming (Field *et al.*, 2006). Currently, there are few high-quality data on the diel vertical distributions of euthecosomes and foraminifera in these areas to test whether shelled pteropod and foraminiferal populations will shift their depth ranges as the carbonate chemistry of seawater changes.

In addition to calcification, other physiological indices indicate general trends that may be useful for predicting species' vulnerability to ocean acidification. Those with low metabolic rates, including perhaps gelatinous zooplankton and those that experience little natural variation in CO_2, appear to demonstrate lesser CO_2 tolerance. Thus, at first glance, zooplankton inhabiting the open ocean may appear highly susceptible to ocean acidification, given the constancy of the pelagic environment relative to hydrothermal vents or the intertidal zone (Truchot and Duhamel-Jouve, 1980). However, large, vertical gradients in environmental variables, including oxygen, CO_2, and pH, exist in the upper 1000 m (Figure 3), and most zooplankton species migrate daily from near-surface waters to depths of 200–700 m. In the expansive regions with pronounced oxygen minimum layers (Figure 3c), these diel migrations expose zooplankton to wide variations in pCO_2, values (Figure 3b) greater than those expected for average surface waters as a result of anthropogenic ocean acidification over the next 100 years (Figure 1). Therefore, although the open ocean environment has fluctuated historically only over millennial time-scales (Kennett and Ingram, 1995), giving species ample time to adapt (Childress and Seibel, 1998), the effective environment of many species in the open ocean is not constant.

Many species migrating into oxygen minimum layers may do so by suppressing metabolism and supplementing remaining energy demands with anaerobic metabolic pathways (Childress and Seibel, 1998; Hunt and Seibel, 2000). Anaerobic metabolism itself may exacerbate internal acid–base imbalance (Hochachka and Somero, 2002). Therefore, vertically migrating species, like those living intertidally or near hydrothermal vents, experience oscillating periods of simultaneous hypoxia and high pCO_2 that require specific adaptations for tolerance (Childress and Seibel, 1998). Those adaptations may make zooplankton in hypoxic regions more tolerant of elevated pCO_2, at least on short time-scales, than those in well-oxygenated regions. This hypothesis is supported by the recent work of Watanabe *et al.* (2006), who found greater mortality during short-term exposure to high pCO_2 in shallow-living and subtropical copepods than in deep-living species in the Subarctic Pacific, where pCO_2 is naturally much higher. However, Pane and Barry (2007) suggested that low oxygen exacerbated internal acid–base imbalance in a

deep-sea crab. Currently, there is no evidence that adaptation to variably hypercapnic environments promotes tolerance of chronic ocean acidification such as that expected over the next century. Furthermore, as warming alters ocean stratification, the vertical and horizontal extent of the oxygen minimum layer is expected to change, and ocean acidification will elevate pCO_2 levels at subsurface depths. Warming is also expected to act synergistically to exacerbate oxygen limitation and further hinder CO_2 tolerance (Metzger *et al*., 2007).

Predictive ability of the response of zooplankton populations to ocean acidification is hampered by a paucity of measurements at climate-relevant CO_2 concentrations (Table 1). In many cases, no information exists for ecologically important taxa such as larvaceans, salps, amphipods, and euphausiids. Gelatinous zooplankton have not been examined at all for CO_2 tolerance. Their low metabolic rates may make them highly susceptible; however, they may also exhibit species-specific responses to increased pCO_2, similar to the differential response observed among medusae species to hypoxia (Rutherford and Thuesen, 2005; Thuesen *et al*., 2005a, b). Attrill *et al.* (2007) reported a significant correlative relationship between reduced pH and increased frequency of medusae, as sampled by the Continuous Plankton Recorder for 40 years in the North Sea. The authors suggest that the frequency of medusae in the North Sea will increase over the next century as surface water pH values decrease. As yet, no causative mechanism linking jellyfish abundance with ocean acidification is known.

Fertilization success and early developmental stages of many faunal groups appear to be particularly vulnerable to elevated pCO_2 (Table 1). The tolerance of early life stages may impact recruitment success and, ultimately, species abundances and distributions. If the formation of highly soluble, amorphous $CaCO_3$ as a transient precursor to crystalline phases in embryonic and larval stages (Beniash *et al*., 1997; Weiss *et al*., 2002) is widespread among mollusc and echinoderm species, then these phyla may be particularly at risk from progressive ocean acidification in many oceanic regions. Additional investigation is needed to determine if ocean acidification-induced mortality of these stages could drive a reorganization of benthic and pelagic communities and also adversely impact commercially important fisheries.

Trophic dynamics and other ecosystem processes

The relative rate of change in surface seawater carbonate ion concentration is greatest in high-latitude regions (Orr *et al*., 2005; Figure 4). In polar and subpolar areas, the progressive shoaling of the aragonite saturation horizon and the decreasing calcite saturation state of the euphotic zone over future decades will impact trophic dynamics and other ecosystem processes, including the cycling of $CaCO_3$ and organic matter. Euthecosomatous pteropods are functionally important components of high-latitude ecosystems with the potential to influence phytoplankton stocks (Hopkins, 1987), carbon fluxes (Noji *et al*., 1997; Collier *et al*., 2000; Honjo *et al*., 2000), and dimethyl sulphide levels (Levasseur *et al*., 1994) that, in turn, influence global climate through ocean–atmosphere feedback loops. The possible extirpation of euthecosomatous pteropods from the high-latitude regions would impact the downward organic carbon flux associated with pteropod faecal pellets (Thibault *et al*., 1999; Collier *et al*., 2000) and remove a major source of $CaCO_3$ in such regions (e.g. Bathmann *et al*., 1991; Gardner *et al*., 2000; Honjo *et al*., 2000; Accornero *et al*., 2003; Tsurumi *et al*., 2005). Similarly, if foraminifera densities decrease in some high-latitude regions, where they are currently abundant (e.g. Subarctic Pacific), $CaCO_3$ export to the ocean interior will be reduced, which in turn would decrease their potential to act as ballast in the transport of organic carbon to the deep sea (Schiebel, 2002).

Most of the carnivorous zooplankton and fish (e.g. cod, pollock, haddock, mackerel) that feed on euthecosomatous pteropods (Ito, 1964; LeBrasseur, 1966; Lalli and Gilmer, 1989) would be able to switch to other prey types, which could result in greater predation pressure on juvenile fish such as salmon (Willette *et al*., 2001). In contrast, gymnosomes prey exclusively on shelled pteropods (Lalli and Gilmer, 1989) and would likely shift their geographic distribution in concert with their euthecosome prey, assuming both predator and prey are able to overcome possible thermal tolerance limitations (Seibel *et al*., 2007). Another specialized predator, the myctophid *Centrobrachus brevirostris*, which feeds predominantly on the pteropod *C. pyramidata* in the Kuroshio waters of the western North Pacific (Watanabe *et al*., 2002), would also be highly impacted if euthecosomes were excluded from its habitat in the future; typically, the trade-off in such highly specialized feeding is a reduced ability to diversify when the preferred prey is absent.

In the North Pacific, the euthecosomes *L. helicina* and, to a lesser extent, *C. pyramidata* can be important prey of juvenile pink salmon (*Oncorhynchus gobuscha*), which comprise a large part of the commercial catch of salmon in the North Pacific (cf. Armstrong *et al*., 2005). Pink salmon have a short, two-year lifespan, and their recruitment is thought to be affected by diet and availability of prey during their early marine life history. In a three-year study designed to examine the interannual variability of the feeding habits of juvenile pink salmon, Armstrong *et al.* (2005) found that *L. helicina* accounted for $\geq$60% by weight of the juvenile salmon diet in two of three years, but only 15% in the third year. Juvenile pink salmon rapidly increase in size during summer in the Subarctic Pacific, feeding on progressively larger prey items and switching from *L. helicina* to the larger *C. pyramidata* by October (Boldt and Haldorson, 2003; Armstrong *et al*., 2005). In a model study linking oceanic foodwebs to production and growth rates of pink salmon, Aydin *et al.* (2005) found that decreased energetic foraging costs for zooplanktivorous juvenile salmon and the ontogenetic diet shift from zooplankton to squid were both key factors that strongly influenced the biomass of mature pink salmon. Because euthecosomatous pteropods can reach swarm densities in near-surface waters during daylight, either through concentration by eddies (Tsurumi *et al*., 2005) or life-history traits (Bathmann *et al*., 1991; Gannefors *et al*., 2005), visual predators such as juvenile pink salmon may be able to reduce forage costs by feeding within pteropod patches. Other preliminary model results suggest that a 10% decrease in pteropod production could lead to a 20% drop in mature pink salmon body weight (Aydin, pers. comm.). During the ontogenetic diet shift of juvenile salmon, the gonatid squid *Berrytheuthis anonychus* is an important control on adult salmon biomass; availability of this lipid-rich prey species substantially accelerates the growth of both pink and sockeye salmon in bioenergetics models (cf. Aydin *et al*., 2005). Similarly, *Gonatus fabricii*, among the most abundant squid species in the North Atlantic, is the most important prey item to a number of marine mammals and may be responsible for their seasonal occurrence in some regions (Bjorke, 2001; Hooker *et al*., 2001). Although the respiratory physiology of gonatid squid has not been investigated in detail, their metabolic

rates are high (Seibel, 2007), which may lead to high CO_2 sensitivity, as described above for ommastrephids (e.g. Pörtner and Reipschläger, 1996; Pörtner *et al.*, 2004). Ommastrephids are also important components of ecosystems and are important commercial fisheries worldwide (Rodhouse and White, 1995; Clarke, 1996; Nigmatullin *et al.*, 2001).

Ocean acidification could also affect foodwebs and carbon cycling through bottom-up controls involving pH-dependent speciation of nutrients and metals (Huesemann *et al.*, 2002), which, in turn, may alter species composition and rates of primary productivity. The interactive effects and feedback of changing seawater CO_2 chemistry with other stressors, such as warming, eutrophication, introduced species, and overfishing, may act to alter ecosystem responses that would otherwise result from only one of these stressors (Schippers *et al.*, 2004; Hutchins *et al.*, 2007). Quantification of these complex ecosystem processes requires additional empirical data, as well as new modelling efforts, particularly on regional scales.

Research needs and conclusions

Most experimental work on the impacts of ocean acidification on marine biota at climate-relevant pCO_2 values has investigated the calcification response of corals and coccolithophores (cf. Kleypas *et al.*, 2006). There is a critical need for information on the sublethal calcification and energetic responses of a diverse suite of zooplankton and micronekton. We need to move forward on several fronts in parallel.

- In sensitive regions and for critical species, we need to track the abundances and depth distributions of calcareous and non-calcifying fauna, measure calcification and metabolic rates of these groups, and relate these data to changes in the CO_2 chemistry of the water column. This requires commitment to long-term monitoring programmes at appropriate temporal and spatial scales to detect possible shifts, and distinguish between natural variability and anthropogenically induced changes.
- Using pCO_2 levels projected to occur over the next century, manipulative laboratory experiments are needed to investigate the calcification and dissolution responses, identify physiological indices useful in predicting CO_2 tolerance, determine the costs of acid–base regulation, and quantify sensitive energetic processes, such as skeletal and tissue growth, reproduction, and metabolism for critical life stages of key species.
- Mesocosm and field experiments are necessary to quantify ecosystem impacts from ocean acidification that may include forcing from bottom-up controls, changes in foodweb structure, biogeochemical cycling, and feedback mechanisms.
- High-priority areas for research include high-latitude regions, which may become undersaturated with respect to aragonite as early as 2050, and regions with pronounced oxygen minimum layers or coastal hypoxia, which are already characterized by high pCO_2 and may be particularly at risk, owing to the combined effects of low oxygen with elevated pCO_2, warming, and eutrophication.
- Target species for investigation in the above regions include euthecosomatous pteropods, foraminifera, epipelagic squid, and larval stages and adults of commercially and ecologically important benthic invertebrates such as bivalves, sea urchins, crabs, and lobsters. We also need to test taxa for which there are currently no data available, including medusae, larvaceans, and various crustaceans. Additional experiments should examine the interactive effects of seawater CO_2 chemistry with temperature, dissolved oxygen, food availability, and other variables that may change as a result of human activities.
- New approaches (e.g. functional genomics and DNA barcoding) and advances in existing technologies (e.g. autonomous chemical sensors and optical plankton samplers) are necessary to investigate the *in situ* response of organisms that are difficult to maintain in the laboratory, identify sublethal effects of chronic exposure to elevated pCO_2 on marine fauna, and address questions of long-term impacts and potential for adaptation over decadal to centennial time-scales.
- Models are critical to scale up results from manipulative experiments and field observations to predict ecosystem impacts on regional and global scales.

Although the changes in seawater chemistry that result from the oceanic uptake of anthropogenic CO_2 are well characterized over most of the ocean, the biological impacts of ocean acidification on marine fauna are only beginning to be understood. New technologies and advances, as well as integrated, multidisciplinary efforts among biologists and chemists, experimentalists and modellers will be required to quantify the effects of ocean acidification on marine fauna and changes in ecosystem structure and function. Nevertheless, sufficient information exists to state with certainty that deleterious impacts on some marine species are unavoidable, and that substantial alteration of marine ecosystems is likely over the next century.

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