Marine Climate Change in Australia Impacts and Adaptation Responses 2012 REPORT CARD

Ocean acidification

William R. Howard¹, Merinda Nash², Ken Anthony³, Katherine Schmutter⁴, Helen Bostock⁵, Donald Bromhead⁶, Maria Byrne⁷, Kim Currie⁵, Guillermo Diaz-Pulido⁸, Stephen Eggins⁹, Michael Ellwood⁹, Bradley Eyre¹⁰, Ralf Haese¹¹, Gustaaf Hallegraeff¹², Katy Hill¹³, Catriona Hurd¹⁴, Cliff Law⁵, Andrew Lenton¹⁵, Richard Matear¹⁵, Ben McNeil¹⁶, Malcolm McCulloch¹⁷, Marius N. Müller¹², Philip Munday¹⁸, Bradley Opdyke⁹, John M. Pandolfi¹⁹, Russell Richards²⁰, Donna Roberts²¹, Bayden D. Russell²², Abigail M. Smith²³, Bronte Tilbrook¹⁵, Anya Waite¹⁷, Jane Williamson²⁴

¹Australian National University and Office of the Chief Scientist, GPO Box 9839, Canberra ACT 2601

²Research School of Physics, Australian National University, ACT 0200

³Australian Institute of Marine Science, PMB 3, Townsville, QLD 4810

⁴52 Bimberi Crescent Palmerston ACT

⁵National Institute of Water and Atmospheric Research, Private Bag 14-901, Kilbirnie, Wellington 6002, New Zealand

⁶Oceanic Fisheries Programme, Secretariat of the Pacific Community, Noumea, New Caledonia

⁷School of Medical and Biological Sciences, University of Sydney, Sydney NSW 2006
 ⁸Griffith School of Environment & Australian Rivers Institute - Coast & Estuaries, Griffith University, 170 Kessels Road, Brisbane, Nathan OLD 4111

⁹Research School of Earth Sciences, Australian National University, ACT 0200

¹⁰Southern Cross University, Lismore NSW 2480

¹¹Geoscience Australia, GPO Box 378 Canberra ACT 2601

¹²Institute for Marine and Antarctic Studies, University of Tasmania, Hobart TAS 7001

- ¹³Integrated Marine Observing System, University of Tasmania, Hobart TAS 7001
- ¹⁴Department of Botany, University of Otago, PO Box 56, Dunedin, NZ

¹⁵CSIRO Marine and Atmospheric Research, Hobart, TAS 7001

¹⁶Climate Change Research Centre, University of New South Wales Sydney, NSW 2052

¹⁷Oceans Institute, University of Western Australia, Crawley, WA 6009

¹⁸ARC Centre of Excellence for Coral Reef Studies and School of Marine and Tropical Biology, James Cook University Townsville QLD

¹⁹ARC Centre of Excellence for Coral Reef Studies and School of Biological Sciences, The University of Queensland, St. Lucia, Queensland 4072

²⁰Centre for Coastal Management, Griffith University, Gold Coast, Queensland 4222

^{21A}ntarctic Climate & Ecosystems Cooperative Research Centre, University of Tasmania, Hobart, TAS 7001

²²Southern Seas Ecology Laboratories, School of Earth and Environmental Sciences, University of Adelaide, SA 500

²³Department of Marine Science, University of Otago, Dunedin, NZ

²⁴School of Biological Sciences, Macquarie University, Sydney, NSW 2109

Howard, W.R., et al. (2012) Ocean acidification. In A Marine Climate Change Impacts and Adaptation Report Card for Australia 2012 (Eds. E.S. Poloczanska, A.J. Hobday and A.J. Richardson). http://www.oceanclimatechange.org.au>.

Introduction

Context and purpose

Increasing atmospheric CO_2 concentration is causing increased absorption of CO_2 by the world's oceans, in turn driving a decline in seawater pH and changes in ocean carbonate chemistry that are collectively referred to as **ocean acidification**. Evidence is accumulating to suggest ocean acidification may directly or indirectly affect many marine organisms and ecosystems, some of which may also hold significant social and economic value to the Australian community.

This report card aims to provide a brief overview of the current state of scientific knowledge regarding the process of ocean acidification; current and future projected levels of ocean acidification; and, observed and projected impacts of current and future predicted levels of ocean acidification on marine organisms and ecosystems in the region. This Report Card also briefly discusses potential social and economic implications, policy challenges, and the key knowledge gaps needing to be addressed.

What is ocean acidification?

Anthropogenic CO₂ emissions arising from fossil-fuel combustion, land-use practices, and concrete production during and since the industrial revolution first enter the atmosphere, but a large proportion of are absorbed into the ocean by physical and biological processes that are normal parts of the natural carbon cycle. These emissions have resulted in a ~40% increase in atmospheric CO2 concentrations over pre-industrial levels [Tans and Keeling, 2011]. Over the same period, the ocean has absorbed approximately 30%-50% of these emissions [Sabine et al., 2004; Sabine and Tanhua, 2010]. Although the absorption of anthropogenic CO2 by the ocean has provided a degree of buffering against global warming (which results largely from increased CO2 in the atmosphere), the increase in dissolved CO2 is accompanied by chemical reactions that increase oceanic hydrogen ion concentrations (thus reducing seawater pH) and bicarbonate ion concentrations while reducing carbonate ion concentrations.

The result is more CO₂ dissolved in the world's oceans. Seawater is a weakly-alkaline solution (with a pH of ~ 8.1), but this extra CO₂ changes the carbonate chemistry of the surface ocean, driving ocean pH and carbonate ion concentrations lower. While the relative acidity or alkalinity of seawater (typically measured as pH) shows significant spatial and temporal variation throughout the world's oceans, seawater is on average a weakly-alkaline solution (with a mean pH of ~ 8.1). Ocean acidification is estimated to have lowered the mean pH of the ocean from its pre-industrial state by about 0.1 pH units [Friedrich et al., 2012]. The declining trend in pH has been verified in recent decades by measurements e.g. [Byrne et al., 2010; Doney et al., 2009].

The process of ocean acidification is already underway and discernible in the ocean [Feely et al., 2004]. By the end of this century pH levels are likely to drop 0.2 - 0.3 units below pre-industrial pH. The level of atmospheric CO₂ is now higher than at any time in at least the past 650,000 years, and probably has not been as high as present levels for approximately 4-5 million years [Hönisch et al., 2012; Pagani et al., 2010]. The current rate of increase of CO₂ in the atmosphere is one hundred times greater than the most rapid increases during major climate changes over the last 650,000 years, and the concomitant rate of carbonate chemistry change in the ocean is similarly rapid [Friedrich et al., 2012; Lüthi et al., 2008; Midorikawa et al., 2012].

Nearly half the fossil-fuel CO_2 emitted to date has now dissolved into the ocean[Le Quéré et al., 2009; Sabine et al., 2004].

 CO_2 - driven acidification, in addition to lowering seawater pH, shifts the proportion of dissolved carbon dioxide away from carbonate ion and to bicarbonate ion, and thus towards lower saturation states for carbonate mineral. Calcium carbonate precipitation at a decreased saturation state requires higher energetic demands from shell-making organisms.

Why is ocean acidification a concern?

The marine environment is home to a vast and diverse range of organisms and ecosystems, all of which will directly or indirectly experience, to a greater or lesser degree, changes in ocean chemistry associated with ocean acidification. For many marine organisms, marine carbonate chemistry and pH are known to play important roles in key physiological processes (e.g. calcification in corals and shellfish, acid/base balance, fertilisation etc) that ultimately influence their behaviour, growth, development and/or survival. Some research suggests that ocean acidification has already begun to have detectable impacts on some biological processes.

Most conclusions about biological responses to ocean acidification in Australian waters come from laboratory manipulations rather than in situ observations. However there is observational data documenting already-underway changes in calcification in Southern Ocean zooplankton [Moy et al., 2009; Roberts et al., 2011] and in Great Barrier Reef corals [Cooper et al., 2008; De'ath et al., 2009]. Though unambiguous attribution of these observed trends to acidification is still uncertain, they suggest acidification may have already begun to have detectable impacts on biological processes.

Similarly, a range of physiological processes are sensitive to pH itself. Changing pH also influences other important aspects of seawater chemistry, such as the availability of nitrogen and iron (both necessary for marine plant production) [Shi et al., 2010].

Given that a significant proportion of the global (including Australian) human population is directly or indirectly reliant on the ecosystem services provided by the ocean (e.g. for food security, employment, tourism), many governments are becoming increasingly concerned with understanding the likely ecological, economic and social implications of ocean acidification

There are a number of key questions that must be addressed to inform decisions regarding the management of, and response to, this issue in the short and long term:

- 1. What is the current degree of acidification and what level is it predicted to reach in the short, medium and long term, a range of anticipated global carbon emission scenarios?
- 2. Which organisms and ecosystems have been or will be impacted by ocean acidification? How soon will impacts manifest themselves and are any species or ecosystems likely to benefit?
- 3. How will ocean acidification interact with other ecosystem stressors (e.g. pollution, overfishing, ocean warming, hypoxia, etc.)

- 4. What capacity might organisms have to adapt to ocean acidification (i.e. via natural selection of resistant individuals over relevant timeframes)?
- 5. What are the social and economic implications of ocean acidification impacts?
- 6. What policy response is required?

The level of research into and understanding of ocean acidification and it potential biological impacts is growing rapidly. The following sections summarise the current state of scientific knowledge pertaining to observed and predicted changes in ocean chemistry and biological processes resulting from ocean acidification, with special emphasis on studies relevant to the Australasian region. This review is intended to highlight knowledge gaps and facilitate discussion of policy implications and challenges (including social and economic implications).

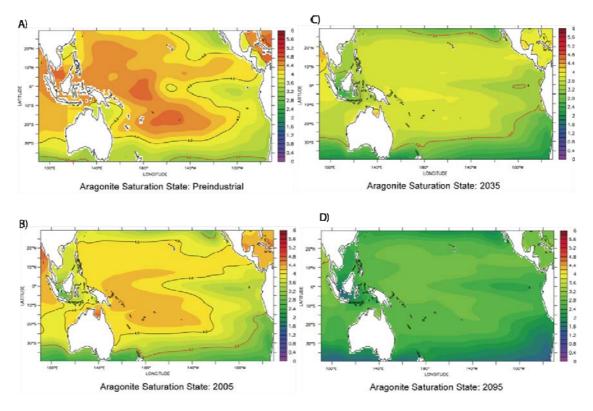


Figure 1. Annual mean aragonite saturation state in the surface water for: a) 1800; b) 2005; c) 2035; d) 2095. For the future years the IS92a atmospheric CO2 concentrations is used along with the CSIRO Mk3.5 climate projection to determine project the aragonite saturation state.

Major scientific knowledge gaps in the physical response lie in several aspects of the physical, biological, and ecological implications of ocean acidification. One area of gap is in projecting the spatial and temporal variability in the progression of acidification. In particular there is a critical need for regional and local-scale data on carbonate chemistry variability. Another major class of knowledge gaps concerns the vulnerability of different organisms and ecosystems. The major scientific knowledge gaps in biological and ecological responses lie in understanding inter-specific and intra-specific differences in response to acidification ("winners" versus "losers") or the ability to internally regulate pH [McCulloch et al., 2012a; McCulloch et al., 2012b], the potential evolutionary adaptation of organisms to acidification[Parker et

al., 2012; Sunday et al., 2011], and in the implications for the structure of ecosystems [Hughen et al., 2004; Hughes et al., 2010; Pandolfi et al., 2011]. Similarly, though much research has focused on marine calcifiers, the impact of shifts in carbonate chemistry on microbial communities and processes is still little understood e.g. [Bowler et al., 2009; Tortell et al., 1997; Witt et al., 2011]

Observed Impacts

Chemical changes to the oceans

High Confidence. The pH of surface oceans has dropped by 0.1 units since the industrial revolution[Feely et al., 2004; Feely et al., 2009]. The carbonate mineral saturation state for calcite and aragonite show decade-scale downward trends[DeVries and Primeau, 2009; Doney et al., 2009; Feely et al., 2012; Matear and McNeil, 2003; Matear and Lenton, 2008; McNeil and Matear, 2008]. Historical pH drops in seawater pH have been inferred using boron isotope proxies in coral archives [Pelejero et al., 2005; Pelejero et al., 2010; Wei et al., 2009].

Biological changes to the oceans

Medium confidence. Calcification rates in Southern Ocean calcareous zooplankton (foraminifera) have dropped 30-35 % since the pre-industrial times[Moy et al., 2009]. Great Barrier Reef corals have reduced calcification rates [De'ath et al., 2009]. Though attribution to ocean acidification alone is unclear (increased sediment runoff and thermal stress are the other likely causes), recent declines in GBR-wide coral calcification rates are unprecedented in at least the past 400 years. It is nevertheless clear that changes in the marine environment together with more frequent coral bleaching are reducing coral growth rates. Evidence is emerging of similar declines from other coral reef regions[Tanzil et al., 2009] although some coral reefs distal from terrestrial impacts show greater rates of calcification [Cooper et al., 2012] consistent with the positive enhancement of warming on calcification e.g. [McCulloch et al., 2012a]. Lightly calcified coccolithophores have shifted ranges poleward in recent years. Though attribution to ocean acidification is unclear, the pattern is consistent with the expected impact [Cubillos et al., 2007].

Low confidence. Calcification in pteropods in the Southern Ocean [Roberts et al., 2011] and tropical waters [Roger et al., 2012] has decreased on decadal time scales.

Potential impacts by the 2030s and 2100s

Chemical changes to the oceans

High Confidence. The pH of surface oceans will drop by 0.2 - 0.3 units by ~ 2100). The carbonate mineral saturation states for calcite and aragonite will continue their decade-scale downward trends[Matear and Lenton, 2008]. In areas of high seasonal variability in carbonate chemistry, such as the high-latitude Southern Ocean, aragonite saturation thresholds may be crossed in winter by ~ 2040 [McNeil and Matear, 2008; McNeil et al., 2011].

Medium Confidence. The entire Southern Ocean surface (south of the current Polar Front Zone) will be undersaturated for aragonite by ~ 2100 [Orr et al., 2005]. Tropical

aragonite saturation states will decrease to a level that will prevent optimal coral growth[Kleypas et al., 1999; Orr et al., 2005; Veron et al., 2009]. Aragonite saturation horizons will shoal, especially in the Antarctic and Australian southern margins, threatening a wide range of benthic calcifiers (see below).

Low confidence. pH changes in coastal systems have mirrored changes in the open ocean. There are few long-term records of the CO_2 -carbonate system in shallow coastal systems. In shallow coastal systems there are a number of processes that produce and consume alkalinity that can potentially buffer or enhance the effect of ocean acidification. These include the dissolution of carbonate minerals, sediment denitrification, and reduced sulphur burial. Coastal systems also receive river and groundwater inputs of alkalinity. Alkalinity sinks in coastal systems include precipitation of carbonate minerals, oxidation of reduced sulphides, and coupled nitrogen fixation and aerobic respiration.

Biological changes to the oceans

Medium confidence. Calcification rates in Southern Ocean calcareous zooplankton (foraminifera) are likely to continue to decline [Moy et al., 2009] and impacts on pteropods are likely to emerge [Fabry et al., 2008]. Many taxa of calcifiers especially that are unable to internally manipulate their pH (eg coralline algae and some foraminifera) will experience reduced calcification rates[Anthony et al., 2008; Anthony et al., 2011b; De'ath et al., 2009]. Coral growth is likely to be affected by multiple impacts of ocean warming, bleaching and acidification [Erez et al., 2011; Hobday and Lough, 2011; Hoegh-Guldberg, 2005; Hoegh-Guldberg et al., 2007; Lough and Cooper, 2011; Lough and Hobday, 2011; Silverman et al., 2007; Silverman et al., 2009]. However, corals show a diversity of responses to acidification, and overall responses or reef ecosystems are likely to be complex. In particular some marine organisms may have evolutionary time scales short enough to adapt to acidification on decadal to centennial time scales e.g. [Sunday et al., 2011].

Many mid- and high-latitude benthic calcifiers such as deep-water and cold-water corals[Guinotte et al., 2006; Maier et al., 2009], coralline algae e.g. [Martin et al., 2008; Martin and Gattuso, 2009; Russell et al., 2009; Russell et al., 2011b], bryozoans [Smith, 2009; Smith and Lawton, 2010] and other benthic calcifiers [McClintock et al., 2009] are likely to show the effects of increased dissolution on their exposed carbonate skeletons as aragonite saturation horizons shoal [McCulloch et al., 2012b]. The effects on calcification will variable, dependent on species specific internal processes to modulate pH regulation and likely enhancement of calcification from warming of cold-water environments [McCulloch et al., 2012a].

Economically important taxa such as shellfish may show reduced growth and/or calcification [Barton et al., 2012].

Ecosystems will show signs of restructuring as changes to ecosystem services like calcification alter benthic substrata, and to the extent non-calcifiers are advantaged.

Low confidence. Possible reduction in fertilisation in some marine invertebrates [Havenhand et al., 2008; Havenhand and Schlegel, 2009; Parker et al., 200

al., 2012], but not others [Byrne, 2012]. Some reef fishes may experience impaired olfactory-based navigation under lower pH, hindering their ability to find suitable habitats[Munday et al., 2009b].

Overall responses of fish taxa may be highly varied and thus difficult to simply predict, but have significant implications for economically-important ecosystems and fisheries. Experimental evidence available to date suggests ocean acidification is not likely to have significant direct effects on the growth, development and survival of most adult fish taxa. However elevated CO_2 may affect sensory systems and behaviour. Recruitment adult populations would decline if increased mortality of larvae and juveniles results from acidification. Reduced aerobic capacity in some fish could exacerbate climate change impacts.

Low confidence. pH changes in coastal systems will mirror predicted changes in the open ocean. Shallow coastal systems have a number of alkalinity sources and sinks that may potentially buffer against, or enhance, ocean acidification (see above). In addition, other stressors such as eutrophication and hypoxia will also interact with ocean acidification to modify its effect in shallow coastal systems.

Adaptation Responses

The likely peak of atmospheric carbon dioxide levels well above present concentrations, even with emissions-reduction measures, means ocean acidification impacts will be inevitable and marine ecosystem management strategies (e.g. marine protected areas) will have to factor in some acidification impacts.

Knowledge Gaps

There exist a number of important scientific knowledge gaps pertaining to the response of physical and biological systems to ocean acidification. These gaps also hinder our ability to understand the social and economic implications and hinder the capacity of decision makers to develop appropriate policy responses. Key knowledge gaps include:

- 1. **Physical/chemical responses:** There is a lack of understanding of future fine scale spatial and temporal variability in the progress of acidification. There is a critical need for regional and local-scale data on carbonate chemistry variability, such as large-amplitude tidal-cycle changes in carbonate chemistry, pH, and net calcification [Hofmann et al., 2011; Santos et al., 2011; Shaw et al., 2012].
- 2. **Biological/ecological responses:** There is a lack of understanding of:
 - a. Inter-specific and intra-specific differences in response to acidification ("winners" versus "losers"). Much research has focused on marine calcifiers, however the impact of shifts in carbonate chemistry on other key ecosystem components, such as microbial communities and processes, is still little understood e.g. [Bowler et al., 2009; Tortell et al., 1997]

- b. The potential for organisms to adapt (via natural selection for more resistant individuals) to changes in ocean chemistry over relatively short time frames [Parker et al., 2012; Sunday et al., 2011].
- c. The implications of ocean acidification for the structure of ecosystems;
- d. The effect of multiple stressors [Byrne, 2011; Ericson et al., 2012; Wernberg et al., 2011], especially the combined impacts of likely environmental changes such as expansion of hypoxic zones and increased temperature [Brewer and Peltzer, 2009; Gruber, 2011] but also of shifting patterns of salinity e.g. [Durack et al., 2012].

Crucially there is a need to scale the understanding of ocean acidification impacts from "narrow" taxon-specific experiments to ecosystem-level experiments. Free Ocean Carbon Enrichment experiments or "FOCE" may provide important insights into ecosystem-level impacts of ocean acidification [Kline et al., 2012]. Ultimately there is a need to detect and reliably attribute ocean acidification impacts in nature. To date there are few in-situ studies that attempt to unravel the effects of ocean acidification (two in Australian waters [De'ath et al., 2009; Moy et al., 2009]) from other compounding factors and there is a need for ecosystem-level impact research [Russell et al., 2011a]. So far insights into ecosystem-level impact come from studies of naturally-acidified systems where CO_2 outgasses through volcanic vents [Fabricius et al., 2011; Hall-Spencer et al., 2008; Tunnicliffe et al., 2009].

Policy implications and adaptation responses

Key policy challenges

The previous sections have identified that:

- a. at its current level, ocean acidification may already be affecting some marine organisms (e.g. foraminifera) and ecosystems (GBR) and
- b. ocean acidification will continue to increase through and beyond the end of this century, thus having the *potential* to have much wider and long-lasting impacts on marine ecosystems.
- c. there remains, however, significant scientific uncertainty regarding the medium- and long-term degree and extent of possible impacts.

Governments are guided by legislation and policy frameworks that define their environmental, economic and social objectives (amongst others). On current evidence and scientific understanding of its observed and potential impacts, ocean acidification may pose a threat to the long term achievement of environmental objectives (an example, in the Australian context, is the Environmental Protection and Biodiversity Conservation Act). Through potential impacts on marine ecosystem services, ocean acidification may also pose risks to economic and social objectives (for example, those associated with maximising economic returns from fishing).

Policy makers are faced with the challenge of obtaining better information pertaining to the risks posed by ocean acidification, and of determining whether and how to develop mitigation and/or adaptation strategies.

Mitigation and adaption considerations

Ocean acidification presents some unique policy as well as scientific challenges. Ocean acidification differs from global warming in that its impact derives from the chemistry of carbon dioxide (CO_2) in seawater, rather than from its physical action as a greenhouse gas in the atmosphere. This means that increasing atmospheric CO_2 will inevitably increase ocean acidity, largely independent of the rate of global warming and its impacts, and independent of climate-model projections. Ocean acidification will need to be considered in the context of setting stabilisation targets for atmospheric CO_2 and the timelines on which the targets need to be reached. There are natural time lags involved in the marine carbon cycle, both in the uptake of CO₂ by the ocean as well as in the centuries needed to reverse the acidification already under way [Archer et al., 2009; Goodwin and Ridgwell, 2010]. These lags place a penalty on delaying limits on carbon emissions and a premium on early action. A further policy challenge arises because the only mitigation options available are reductions in carbon dioxide emissions or some form of carbon dioxide sequestration, or both. Ocean acidification would not be easily ameliorated by most proposed "geoengineering" strategies [Matthews et al., 2009], though some such strategies would specifically act by adding alkalinity and thus buffer the ocean [Kheshgi, 1995; Schuiling and Krijgsman, 2006] The thresholds for atmospheric CO₂ levels at which acidification impacts begin may differ from those which trigger warming impacts, so mitigating acidification may require different emissions-limitation targets than mitigating global warming. Similarly, because acidification arises only from CO₂ emissions, limiting other greenhouse gases (such as nitrous oxide) will not mitigate ocean acidification.

Detailed Assessments of Key Oceanographic and Ecosystem Components, and Processes

Observations and Modelling

The long-term secular changes in carbonate chemistry in the open ocean are now relatively well established [Doney et al., 2009; Doney, 2010]. A key challenge is characterising the progress of acidification in nearshore and shallow marine environments, such as coral lagoons and estuaries. These environments have high natural variability in carbonate chemistry and pH e.g. [Hofmann et al., 2011]. In some shallow-water environments, diurnal (through tidal and sun cycles) variability can exceed the mean decadal-scale change anticipated over the current century [Nguyen et al., 2012; Santos et al., 2011; Shaw et al., 2012], adding complexity to predictions of future carbon chemistry changes under ocean acidification. Bio-geochemical processes and their interaction with ocean acidification are only just starting to be identified and understood. Importantly, there are few baseline carbon chemistry measurements for these shallow environments. Physical changes, including warming, circulation patterns, intensity and frequency of storms, patterns of precipitation and sea level change, may all interact with ocean acidification.

Research is underway in Australia, New Zealand and overseas to improve the methods and equipment used for high-precision carbonate chemistry measurements. One initiative is the development of pH sensors that do not need constant calibration,

which would enable improved consistency of measurements. These could also be used for remote deployment to deliver reliable, high-precision in-situ carbonate chemistry measurements. Another project is currently assessing the possibility of using commonly-measured oceanographic variables (e.g. depth, temperature, salinity and oxygen) to estimate alkalinity and dissolved inorganic carbon. This would enable translation of large-scale and long-term data sets (e.g. satellite estimates of sea-surface temperature) currently collected by the Australian Bureau of Meteorology into pH for large areas of ocean. Alkalinity and DIC will still need to be measured to assess changes in anthropogenic uptake of CO_2 .

Work is being undertaken to identify suitable proxies for carbonate chemistry from sediments, massive corals and coral reef limestone (palaeoceanographic records) that can be used to build a picture of marine carbonate chemistry prior to the Industrial Age. Understanding past changes through geological archives (e.g. deep-sea sediment cores and coral) will provide longer pH and ecological variability records than the historical observational record. In particular the past record of carbonate variability is the only source of documented changes in ocean carbon chemistry of comparable magnitude to those anticipated over the coming decades and centuries.

Monitoring of carbon chemistry in the open marine environment and some shallow coastal systems has already commenced in the Australasian region. The Integrated Marine Observing System (IMOS) delivers and integrates a range of data that contribute to research into ocean acidification¹. Ships and moorings are used to measure CO_2 concentrations in surface ocean waters, and estimate fluxes of CO_2 between the atmosphere and ocean. Wavegliders are also showing potential for taking surface observations. There are currently three coastal carbonate chemistry moorings around the Australian continental shelf, and a time series station in the Southern Ocean. Bi-monthly measurements of marine carbonate chemistry have been made in the surface waters associated with the Subtropical Front of east New Zealand since 1998, and coastal pH is being measured in Wellington Harbour.

The viability of using oceanographic variables other than carbonate parameters themselves as proxies for carbon chemistry patterns and change shows promise for open ocean areas[McNeil et al., 2007; McNeil, 2010]. Spectrophotometric measuring systems, which do not require as much ongoing probe calibration as other systems, have potential for remote deployment in autonomous systems such as moorings and floats [Byrne and Yao, 2008; Martz et al., 2009; Seidel et al., 2008]. A particular observational challenge is represented by alkalinity, an often-utilised parameter for characterising the carbonate system and especially for inferring carbonate precipitation from seawater [Fransson et al., 2011; Ilyina et al., 2009]. The use of commonly-measured oceanographic variables (e.g. temperature, salinity and oxygen) to estimate alkalinity and dissolved inorganic carbon (DIC) in the open ocean may help complement in-situ direct measurements of the carbonate system, especially DIC and alkalinity e.g. [González-Dávila et al., 2010]. These approaches are so far limited in their applicability to shallow-water environments, where biological processes and

¹ IMOS National Science and Implementation Plan http://imos.org.au/plans.html#c1210; IMOS

Observations for Acidification Research, http://imos.org.au/imosobsresearch.html

sediment-water interactions strongly influence seawater carbonate chemistry [Kleypas et al., 2011; Santos et al., 2011]

Proxies of carbonate chemistry from coral and sediment archives are proving useful to reconstruct past carbonate chemistry parameters in order to build a pre-industrial baseline of carbonate chemistry.

Modelling ocean acidification and its impacts faces the challenge of a wide range of spatial scales of variability, spanning from individual organisms to entire ecosystems and spatial scales ranging from local to global extent. Models are now focused on chemical and physical drivers of the carbonate system. Whereas physical transport and atmosphere-ocean fluxes of carbon are mainly well represented in models, pelagic and benthic biological processes and their role in modifying the ocean carbon chemistry are often highly simplified [Hood et al., 2006; Jin et al., 2006; Vichi et al., 2007]. At present, projections of the impacts of ocean acidification cannot be captured by a single model. Rather, hierarchies of models in which spatial, temporal and biological responses at the full range of spatial, ecological, and temporal scales can be separated and investigated are needed. Modelling socio-economic impacts is still in its infancy, however work is underway to extend the known organism-scale impacts of ocean acidification on molluscs to global economics and food security. This work has shown that the potential impacts of declining mollusc growth could be detrimental for some developing nations [Cooley and Doney, 2009; Cooley et al., 2009]. Such socioecological systems modelling is critical to help understand the impacts of ocean acidification on human societies now and in the future.

Calcification processes

One implication of ocean acidification for Australian marine ecosystems is the impact acidification has on the process of calcification - the making of shells, plates and skeletons out of calcium carbonate (CaCO₃) – for the variety of calcifiers important in Australian marine, and global ocean, communities such as corals, shelled plankton and others. Though calcification is only one of many biological processes likely to be affected by acidification, it is an important process in the formation of reef habitats and benthic substrates in a wide range of ecosystems, as well as a key process in the global carbon cycle. In a purely non-biological system, carbonate mineral formation would depend mainly on carbonate ion concentration, e.g. in household "hard water" calcium deposits. Biological calcification, however, is more complex than simple mineral precipitation, given the many biocalcifiers utilizing bicarbonate and metabolic CO_2 e.g. [Roleda et al., 2012] . Acidification affects the rate and energetic cost of calcification, as well as the dissolution of existing skeleton. Many experiments on calcifiers, whether they utilize bicarbonate or carbonate ion, show an apparent dependence of calcification on carbonate ion concentration. However many corals have the ability to up-regulate their internal pH during calcification e.g. [McCulloch et al., 2012a; Venn et al., 2011] and therefore exhibit a lower sensitivity than that predicted from decreases in seawater saturation state alone. The calcification response to increased bicarbonate ion is also complex and variable, and some organisms may be able to take advantage of increased bicarbonate availability to maintain or increase calcification e.g.[Jury et al., 2010; Marubini and Thake, 1999].

The majority of research to date suggests that ocean acidification will reduce overall calcification in calcifying animals in both larval and adult life history stages [Byrne, 2010; Gattuso et al., 2011]. However many experiments suggest mixed impacts of ocean acidification on calcification processes for some organisms [Kroeker et al., 2010; McCulloch et al., 2012a; Miller et al., 2009; Pandolfi et al., 2003; Ries et al., 2009]. The calcifying algae coccolithophores in particular show mixed species and strain-specific responses to acidification [Iglesias-Rodriguez et al., 2008; Riebesell et al., 2000; Riebesell, 2004]. Some of the variable and species-species responses however, are likely to be influenced by variable experimental approaches [Byrne, 2012; Schlegel et al., in press].

Calcification occurs with a variety of physiological mechanisms and in different tissues so generalisations are difficult[Turley et al., 2010]. Some taxa have unprotected external skeletons (e.g. abalone) directly exposed to changing ocean chemistry whereas others (eg. sea urchins) have internal skeletons protected by overlying tissue, a difference that influences vulnerability.[Byrne et al., 2011]. Many scleractinian corals appear to have the ability to up-regulate internal pH which effectively acts to raise their carbonate saturation state at the site of calcification [McCulloch et al., 2012a; Venn et al., 2011]. Species sensitivities and the potential mitigating effects on ocean acidification and energetic costs remain to be investigated. The potential of evolution and adaptation to a changing ocean (mainly in regard to temperature and CO₂/pH) is also not well understood as few experiments have been carried out through multiple generations of organisms. Micro-organisms with short generation times (e.g. bacteria and phytoplankton such as coccolithophores) may be able to genetically adapt to a new environment [Collins and Bell, 2004; Lohbeck et al., 2012; Müller et al., 2010], however evolutionary timescales may vary among larger taxa as well.

Carbonate mineralogy affects the vulnerability of calcification and carbonate net accumulation to ocean acidification. Three calcium carbonate (CaCO₃) polymorphs occur commonly in nature: aragonite, low-magnesium (Mg) calcite (LMC) and high-Mg calcite (HMC; >4mol% MgCO₃) [Andersson et al., 2008]. Aragonite is more soluble than LMC[Mucci, 1983], and HMC with is in turn more soluble than calcite and aragonite [Morse et al., 2007]. Whereas aragonitic organisms are considered the most vulnerable to ocean acidification, high-Mg calcite organisms may be equally, if not more, susceptible. Physiologically, however, aragonite calcifiers may have pH-regulation mechanisms that may confer some resilience to acidification [McCulloch et al., 2012a]

A wide range of marine organisms produce skeletons/shells containing significant amounts of Mg, including echinoderms (2-12mol% Mg), benthic foraminifera (2-16%), coralline algae (7-20%), crustaceans (5-12%) [Chave, 1954]. Some Mg-calcite coralline algae can also form ($Ca_{0.5}Mg_{0.5}CO_3$) and magnesite (MgCO₃) [Nash et al., 2011] and it is not yet understood how rising CO₂ will affect these organisms.

Ocean acidification (OA) leads to reduced concentration of carbonate ions and in turn lowered carbonate mineral saturation states required to maintain shells. Thus OA poses a two-fold problem for species with calcium carbonate structures: (1) Exposed calcium carbonate structures such as shells may start to dissolve if saturation states fall low enough [Rodolfo-Metalpa et al., 2010] and (2) individuals would have to work harder to maintain their shells due to reduced carbonate concentrations in sea water [Cummings et al., 2011], reducing energy available for other processes such as growth and reproduction.

In addition to impacts on calcification, increased levels of pCO_2 , may affect essential physiological processes, such as metabolism and acid-base balance [Langenbuch and Pörtner, 2003; Munday et al., 2009b; Pörtner, 2008; Pörtner and Peck, 2010]. If experimentally-detected physiological responses to acidification occur in nature, they may result in a reduction of fitness for many species with repercussions on ecosystem function. CO_2 -related physiochemistry and ocean warming may work synergistically [Pörtner, 2008].

Corals

Changes in coral reef ecosystems driven by acidification and other impacts, could affect societies that depend upon these ecosystems [Raven et al., 2005]. Calcification in corals throughout the Great Barrier Reef has declined by 14.2% since 1990 [De'ath et al., 2009] and projections of the saturation levels of the form of CaCO₃ precipitated by corals – aragonite – suggest that calcification rates in many warm-water corals may decrease over the next century[Gattuso et al., 1998; Langdon and Atkinson, 2005]. However the joint effects of changing temperature [Cooper et al., 2012], and of internal pH-maintenance mechanisms [McCulloch et al., 2012a] complicate the projection of future acidification to coral growth. Similarly both coral and algal growth can alter seawater chemistry so as to mask or exacerbate the impacts of acidification [Anthony et al., 2011a]. Experiments suggest that ocean acidification will affect coral reefs by mid century, with risks arising both from reduced coral calcification rates in many taxa [Kleypas et al., 1999] and reductions in net community calcification [Silverman et al., 2009]. However, there is a great deal of variability in coral response to acidification and other impacts e.g. [Pandolfi et al., 2011], as well as physiological scope for resilience in calcification for many taxa [McCulloch et al., 2012a]. The impacts of warming-induced bleaching are also of concern [Anthony et al., 2011b]. These major stressors, warming and acidification, do not operate in isolation, with synergistic impacts observed in experiments [Anthony et al., 2008].

Cold-water corals may also experience difficult water chemistry conditions in the coming decades resulting in projected losses as high as 70% by 2100 [Orr et al., 2005] and some as early as 2020 [Guinotte et al., 2006]. Manipulative experiments show that reductions in pH significantly reduce cold-water coral calcification rates (30% and 56% respectively when pH drops by 0.15 and 0.3 units [Maier et al., 2009], however there is potential for acclimation to long-term shifts in carbonate chemistry [Form and Riebesell, 2012]

Holopelagic Calcifiers: coccolithophores, foraminifera, shelled pteropods and other plankton

Impacts on calcification in the planktonic $CaCO_3$ producers – coccolithophores, foraminifera and shelled pteropods – are less well reported but of equal concern given these calcifiers account for nearly all of the export flux of $CaCO_3$ from the upper ocean to the deep sea [Fabry, 2008; Schiebel, 2002].

Coccolithophores – planktonic unicellular shelled algae – are considered to be the most productive calcifying organisms on Earth [Iglesias-Rodriguez et al., 2008; Riebesell et al., 2000] and the cosmopolitan species Emiliania huxleyi is one of the best-studied species in regard to ocean acidification. The process of photosynthetic carbon assimilation may be enhanced in coccolithophores under future ocean acidification [Iglesias-Rodriguez et al., 2008; Riebesell, 2004]. CaCO₃ production on the other hand, shows a diversity responses to increased CO₂ in experiments [Lohbeck et al., 2012]. However, the majority of studies suggest a reduction in calcification in response to ocean acidification [Riebesell and Tortell, 2011], but this appears species- and even strain-specific. However, as with other marine organisms, the combined effects of multiple variables need to be considered [Lefebvre et al., 2011]. Coccolithophores are major contributors to marine primary production, and dominate the vertical supply of CaCO₃ to the deep ocean, and are important components of open ocean and coastal marine ecosystems as well as the global ocean carbon cycle [Balch et al., 2011; Honjo et al., 2008; Iglesias-Rodriguez et al., 2002].

Foraminifera – unicellular shelled protists – are important calcifiers in planktonic and benthic ecosystems [Gooday and Jorissen, 2011; Schiebel, 2002]. Laboratory experiments suggest ocean acidification would reduce calcification in foraminifera, leading to lighter shells[Bijma et al., 2002; Lombard et al., 2010] and recently natural populations of planktonic foraminifera in the Southern Ocean have been found to have 30-35% lighter shells than their counterparts from pre-industrial times [Moy et al., 2009]. Similarly, recent-deposited planktonic foraminifera in Arabian Sea cores also show reduced calcification, also likely due to acidification [de Moel et al., 2009].

Pteropods – planktonic shelled gastropods – can reach densities of more than 10,000 individuals per cubic metre in high-latitude areas[Bathmann et al., 1991; Pane et al., 2004] and are important components of polar food webs, contributing to the diet of carnivorous zooplankton, North Pacific salmon, mackerel, herring, cod and baleen whales[LeBrasseur, 1966; Takeuchi, 1972]. Pteropods also contribute to carbonate fluxes in a range of marine environments[Accornero et al., 2003; Almogi-Labin et al., 1988; Bednarsek et al., 2012; Fabry and Deuser, 1992; Hong and Chen, 2002; Hunt et al., 2008; Jasper and Deuser, 1993; Meinecke and Wefer, 1990; Mohan et al., 2006; Pilskaln et al., 2004; Singh and Conan, 2008; Tsurumi et al., 2005]. Observations of pteropod populations in subantarctic waters since 1997 [Howard et al., 2011] suggest that their numbers and calcification may be declining in these waters [Roberts et al., 2011]. Similarly, observations of shell thickness and porosity in shelled pteropods in tropical Australian waters suggest a decadal reduction in calcification [Roger et al., 2012]. Impacts on calcification processes in these calcifiers is of particular cause for concern as pteropods make shells of aragonite, the more soluble from of CaCO₃ than the calcite produced by coccolithophores and foraminifera, and polar waters in both hemispheres are likely to be especially at risk of aragonite undersaturation by the end of the century [McNeil, 2010; Orr et al., 2005; Steinacher et al., 2009]. Indeed, current laboratory experiments show reductions in pteropod calcification under higher CO₂ [Comeau et al., 2009].

Similarly, experimental data on krill, a key component of the pelagic food web in the Southern Ocean, show impairment of embryonic development at CO_2 levels likely to be seen by the end of this century[Kawaguchi et al., 2010].

Benthic calcifiers: non-coral invertebrates (eg. benthic foraminifera, mollusks and echinoderms)

In addition to corals a large suite of benthic species calcify and some of these such as molluscs and echinoderms are also major habitat providers and play key ecological functions. These groups also include species that calcify across both their planktonic and benthic life history stages. Larval shells are among the smallest and most fragile shells in the ocean, so the vulnerability of calcification in these life stage is of particular concern and is still poorly understood[Byrne, 2011]. Vulnerable early life history stages may be bottlenecks for species persistence[Byrne, 2010; 2011; Dupont et al., 2010].

Benthic foraminifera

Benthic foraminifera are important carbonate producers in many reef environments [Hallock, 2005]. Like their planktonic counterparts a number of benthic foraminiferal taxa show decreased calcification and faunal diversity under elevated CO_2 conditions [Dias et al., 2010; Dissard et al., 2010; Kuroyanagi et al., 2009; Uthicke and Fabricius, 2012]

Molluscs and Echinoderms

Molluscs and echinoderms play key roles in marine habitats by filtering and controlling habitat heterogeneity[Coen et al., 1999; Rodney and Paynter, 2006]. Echinoderms are keystone predators (e.g. sea stars) or grazers (e.g. urchins).

Molluscs and echinoderms are also a key source of food and deleterious effects on commercial species are of great concern. A recent review presents a model of marked production of shell fish in the future due to ocean acidification, at a time when increased human populations and food security will be a considerable challenge[Cooley et al., 2009].

Studies of bivalves and echinoids indicate that larvae reared under ocean acidification and hypercapnia are smaller and have less skeletal material, as well as evident abnormal development [Byrne, 2010; 2011; Dupont et al., 2010; Gazeau et al., 2010; Kurihara, 2008]. The stunting effect of ocean acidification may be caused by impaired calcification under lower mineral saturation conditions, hypercapnic developmental delay/depressed metabolism, teratogenic effects and energetic constraints in acid-base regulation, or a combination of these [Chan et al., 2011; Martin et al., 2011; Sheppard Brennand et al., 2010; Stumpp et al., 2011]. Adult bivalves also show reduced calcification under elevated pCO₂[Gazeau et al., 2007]. Reduced larval size in a high pCO₂ ocean would have a negative impact on feeding and swimming ability and make larvae more vulnerable to predation[Allen, 2008; Przeslawski et al., 2008]. Depending on the species, and perhaps the developmental stage at which experimental incubations are initiated (eg. juveniles, adults[Byrne, 2012]) may also stunt growth of benthic life stages through reduced larval production and midstage growth e.g. [Barton et al., 2012].. Warming (up to a point) may ameliorate the negative effects of acidification on calcifiers by stimulating growth[Byrne, 2011; Sheppard Brennand et al., 2010; Walther et al., 2010]. However some calcifiers may not reach the calcifying larval stage in a warmer ocean[Brierley and Kingsford, 2009]. Non-calcifying

echinoderm larvae appear to be more sensitive to warming than acidification [Nguyen et al., 2012].

Macroalgae

Other important calcifiers include calcareous benthic algae (especially crustose coralline algae or "CCA"s) that precipitate either high-magnesium calcite or aragonite and perform the important function of 'gluing' the skeletons of corals together to create reefs. These organisms' vulnerability to ocean acidification is still being studied but because they can secrete high-Mg calcite they are likely to be affected earlier than other groups of calcifiers [Anthony et al., 2008; Kuffner et al., 2007; McClintock et al., 2009; Nash et al., 2011], and so represent a key area of vulnerability in shelf ecosystems from the tropics to the Antarctic.

Experimental studies in the tropics and temperate localities[Russell et al., 2009] suggest high sensitivity of physiological and population-level processes of CCAs to ocean acidification. In particular, calcification, primary production and abundance are reduced, whereas skeletal dissolution and mortality increase with elevated pCO₂. Interactions with other anthropogenic processes, such as warming and eutrophication, may exacerbate the these responses of calcifying algae[Anthony et al., 2011b; Diaz-Pulido et al., 2012]. Natural experiments with elevated pCO₂ confirm experimental findings[Fabricius et al., 2011; Hall-Spencer et al., 2008]. Upright calcified macroalgae (e.g. Halimeda) are also important producers of sediment to reef environments; these calcifiers' response to acidification also suggest reduced calcification under acidification[Sinutok et al., 2011]. Brown algae, which do not necessarily calcify, but are important carbonate producers in shallow marine ecosystems, also show reduced calcification under elevated pCO₂ near volcanic vents [Johnson et al., 2012]. Elevated pCO₂ may enhance the competitive ability of some seaweeds to overgrowth corals, potentially tipping the balance in favour of non-calcified organisms [Diaz-Pulido et al., 2011].

Key knowledge gaps include: variability in responses across taxa and habitats, potential for adaptation to high CO_2 , identification of molecular, cellular and physiological mechanisms involved in the responses observed, and mineralogical responses.

Impacts on fish

Despite the ecological importance of fishes in marine ecosystems, and their substantial socio-economic significance, relatively little research has been conducted into the effects of ocean acidification on fishes. One risk to fish is the acidosis (high pCO_2 in the bloodstream) induced under exposure to elevated environmental CO_2 , potentially causing acidosis which, at high levels may affect many cellular processes. Fish are generally considered to be more resistant to direct impacts of ocean acidification because they do not have extensive calcium carbonate skeletons. However they have a range of physiological vulnerabilities to elevated p CO_2 and associated changes in ocean chemistry. Impacts may include: reduced respiratory capacity and energetic costs of acid–base maintenance[Munday et al., 2009a; Munday et al., 2009c; Munday et al., 2011a]; impaired sensory performance and altered behaviour[Dixson et al., 2010; Munday et al., 2009b], especially in larval fish; effects

on otolith (earbone) calcification (though in some cases this formation appears to be unaffected or even enhanced[Checkley et al., 2009; Munday et al., 2011b]).

Most of the research in Australia on the impacts of ocean acidification on fish has focused on small coral-reef fishes that are amenable to experimental research, and focused on species that lay their eggs on the substratum (demersal spawners), including many commercially important species. Few studies have examined acidification impacts on species that release their eggs directly into the ocean (broadcast spawners). The latter may represent a critical knowledge gap - eggs and larvae of broadcast spawners may be more sensitive to elevated CO_2 if they develop in the open ocean where CO_2 is more stable than in shallow-water environments. Similarly, pelagic fishes may be more sensitive to elevated CO_2 if they are similarly adapted to stable CO_2 chemistry in the open ocean [Munday et al., 2008].

Previous studies show that the mortality of adult fishes is not directly affected by small increases in ambient CO_2 . Similarly, fertilization and egg survival appears to be tolerant to high CO_2 , at least in the species studied to date. Recent experimental results indicate that the growth and development of larval and juvenile reef fishes is also relatively unaffected by CO_2 levels that might be experienced in the ocean by the end of this century[Munday et al., 2009c; Munday et al., 2011a]. Whether growth and development of species from other habitats, especially pelagic species, are similarly tolerant is unknown. Calcification of otoliths does not appear to be retarded by CO_2 , possibly due to changed bicarbonate concentrations from acid-base compensation.

Fish exposed to high CO_2 exhibit behavioural changes and sensory impairment that affects their capacity to detect appropriate habitats and avoid predators [Domenici et al., 2012; Ferrari et al., 2011; Munday et al., 2009b; Munday et al., 2010; Simpson et al., 2011]. Field experiments show that these behavioural changes could increase mortality rates of newly recruited fish and could lower population replenishment and affect patterns of population connectivity.

Elevated CO_2 has been shown to reduce respiratory capacity in some reef fishes, but the ecological consequences are currently unknown, but one consequence could be reduced metabolic scope needed in a warmer ocean [Pörtner, 2008; 2010; Pörtner and Farrell, 2008]. In general, the metabolic performance of species and life stages with high oxygen demand, such as pelagic species and pelagic larvae, are predicted to be most sensitive to elevated oceanic CO_2 levels.

Microbial Processes

The impact of shifts in carbonate chemistry on microbial communities and processes is still little understood e.g. [Bowler et al., 2009; Joint et al., 2011; Tortell et al., 1997; Witt et al., 2011]. However, a number of studies, including those carried out in NZ waters, have identified an increase in the activity of bacterial extracellular enzymes which indicates a potential increase in the breakdown of organic matter e.g. [Piontek et al., 2010]. Increasing seawater pCO_2 also stimulates fixation of nitrogen (N₂) by cyanobacteria in some experiments e.g. [Hutchins et al., 2009] though not in all cases [Law et al., 2012]. Possible reductions in nitrification under acidification may limit the the supply of nitrate by this microbial pathway [Hutchins et al., 2009].

Paleoceanographic perspective and buffering by deep-sea and shelf carbonate sediments

The injection of carbon to the ocean during the Paleocene-Eocene Thermal Maximum, with its associated acidification and carbonate dissolution, is often cited as an "analog" to the current acidification of the ocean[Hönisch et al., 2012; Leon-Rodriguez and Dickens, 2010; Ridgwell and Schmidt, 2010; Zachos et al., 2005]. The glacial-interglacial cycles of the Late Pleistocene also provide constraints on the response of marine ecosystems to repeated changes in carbonate chemistry of similar magnitude to anthropogenic acidification of the ocean to date[Hönisch and Hemming, 2005; Hönisch et al., 2009].

The response of calcite-dominated deep-sea sediments will depend on their eventual exposure to undersaturated water as fossil-fuel CO_2 penetrates the deep ocean. The depth to which the fossil-fuel carbon dioxide must be absorbed is a function of the calcite saturation horizon and its manifestation in carbonate dissolution. The CSH varies from 3100-2800 m in the basins of the SW Pacific[Bostock et al., 2011]. Evidence from sedimentary cores suggests calcite saturation has varied over glacial/interglacial cycles. In the Pacific Ocean CaCO₃ concentrations are greatest during the deglaciations and lowest during the transition from interglacial to glacial [Farrell and Prell, 1989; Hodell et al., 2001; Marchitto et al., 2005], whereas in the Atlantic and parts of the Southern Ocean carbonate concentrations are highest in interglacials[Crowley, 1983; Howard and Prell, 1994]. The processes responsible for this variability have been debated over the last 50 years and are focused around production versus preservation driven by both ocean circulation-driven partitioning and shelf-basin partitioning in carbonate deposition e.g. [Berger, 1970; Opdyke and Walker, 1992]. The underlying cause represents a fundamental link between ocean biogeochemistry and climate change. Models for the glacial ocean have suggested that increasing the global net dissolution rate of sedimentary CaCO₃ by 40% could reduce atmospheric CO₂ to glacial levels[Archer and Maier-Reimer, 1994]. The CaCO₃ content of deep sea sediments, however, is a complex interplay of changes in overlying carbonate production, dilution by terrestrial sediment/biogenic silica, transport by ocean currents, as well as dissolution from low $[CO_3^{2-}]$ deep waters, or corrosive pore waters, from organic matter degradation[Archer, 1996]. Several proxies have been used to assess changes in the carbonate ion concentration of the water column over time including shell weight, foraminiferal shell fragmentation and more recently the development of boron isotopes as proxies for pH and B/Ca ratios as proxies for carbonate ion concentration[Foster, 2008; Rae et al., 2011; Sanyal et al., 1995; Yu et al., 2007]. Reconstructions applying these proxies suggest the glacial ocean was 0.15 pH units higher than in interglacials[Hönisch and Hemming, 2005]. The current average surface ocean pH is ~0.1 units lower than at any time over the past 1 million years. Studies of the rates and distribution of the marine sedimentary response to past carbon cycle change will help inform our understanding of the future buffering of acidification.

The Australian continental shelf is composed of 80 to 100% carbonate in many areas, including unique ecosystems such as the Great Barrier Reef and extensive bryozoan and seagrass communities in the southern margin and in Torres Strait, respectively. The very high carbonate content reflects the contribution of calcifying organisms to ecosystem diversity and functioning. Calcification provides a key ecosystem service,

producing hard substrate for sessile organism attachment[Wood, 1995] and by generating reef-stabilizing cements[Manzello et al., 2008]. Calcification produces a range of carbonate mineralogies, with implications for the timing of dissolutionmediated buffering of ocean acidification, with high-Mg calcite being the earliest to dissolve from marine sediments[Andersson et al., 2008]. The diversity of calcification is still being studied[Smith et al., 2006; Smith and Girvan, 2010; Smith and Lawton, 2010], with many taxa showing a range of mineralogies. Recently, dolomite was observed in living coralline algae[Nash et al., 2011] and aragonite in hydrocorals in Antarctica[Riddle et al., 2008]. Though dolomite is stable in the marine environment it is, in principle, thermodynamically unlikely to form in these environments. A recent pilot study found high Mg-calcite to be the most abundant carbonate mineral in four northern Australian shelf regions with abundances between 35 and 50% (unpubl. data, R. Haese). As calcification of this mineral fraction is predicted to cease within this century due to ocean acidification, the implications for shelf habitats are profound[Andersson et al., 2007]. Sediment porewater chemistry also represents a still poorly-understood source of feedback processes to acidification especially the interaction with advection in permeable carbonate sediments [Santos et al., 2011] and high diurnal variability in reef environments[Shaw et al., 2012]. Extending the mapping of carbonate mineral distribution and predictions of future mineral stability to other continental shelf regions will assist in establishing a spatial context to changes in calcification and identifying the most threatened ecosystems.

Research Priorities

While pH changes in the open ocean are relatively predictable and now welldocumented, less is known about natural variations in the carbonate chemistry of shallow coastal systems and how these systems might respond to ocean acidification. The coast is dynamic so projections for the oceans can only partially guide what will happen to coastal regions, although an overall depression of pH levels from current baseline conditions seems likely e.g.[Christensen et al., 2011; McElroy et al., 2012]. We urgently need baseline observations of the carbonate chemistry of a range of shallow coastal systems with different sources and sinks of alkalinity. This fundamental information on the CO₂-carbonate system of coastal systems is essential to inform ocean acidification experiments with marine organisms.

Ocean acidification has the potential to significantly affect calcification and a range of other processes in economically significant habitats (e.g., coral reefs, oyster beds), food webs, regionally important ecosystems (e.g. Southern Ocean pteropods) and with implications for planetary geochemical cycles (e.g. through corals, foraminifera, coccolithophores). However, our present understanding of the impact of ocean acidification on physiological processes is informed largely from short-term laboratory experiments whilst we currently know very little about the response of individual organisms, populations, and communities in natural settings and under gradual change scenarios[Doney et al., 2009]. Along with observations of carbonate chemistry. There is a need for baseline observations of important marine populations and wider community responses to acidification in key Australian marine ecosystems (e.g. Southern Ocean, Great Barrier Reef). In concert with this fundamental research, we need to understand how impacts on calcification and other processes will affect the overall structure and function of entire ecosystems and what the consequences of significant changes are

likely to be in terms of those ecosystems especially important to the millions of Australians that depend on them for food, livelihoods, and tourism.

We also need to understand the potential for acclimatization (phenotypic plasticity) and evolutionary (genetic) adaptation of organisms to ocean change stressors especially for ecologically and economically important taxa. There are several major gaps in knowledge. A better understanding of the molecular and cellular mechanisms underlying the responses to will allow us to discern levels of perturbation. Determination of potential for evolutionary change will require targeted genetic e.g. [Sunday et al., 2011] and multigenerational studies e.g. [Lohbeck et al., 2012].

Recommendations

Efforts need to focus on establishing a better understanding of the various calcification processes at different parts of the life cycle for key marine calcifiers and how these are expressed on community and ecosystem levels. We need more information on how non-calcifiers may respond to ocean acidification. The impacts of ocean warming and other impacts in multi-stressor studies are also important to consider.

Ecosystem approaches required include establishing baselines of current calcifiers population 'health', and monitoring in key areas (e.g. Southern Ocean, Great Barrier Reef, temperate systems such as the Great Australian Bight) as well as targeted laboratory process studies, manipulative experiments, community and ecosystem scale mesocosm and free ocean carbon dioxide enrichments (FOCE) experiments and ocean acidification model development on a range of temporal and spatial scales.

References

- Accornero, A., C. Manno, F. Esposito, and M. C. Gambi (2003), The vertical flux of particulate matter in the polynya of Terra Nova Bay. Part II. Biological components, *Antarct. Sci.*, 15(02), 175-188, doi:doi:10.1017/S0954102003001214.
- Allen, J. D. (2008), Size-Specific Predation on Marine Invertebrate Larvae, *The Biological Bulletin*, 214(1), 42-49
- Almogi-Labin, A., C. Hemleben, and W. G. Deuser (1988), Seasonal variation in the flux of euthecosomatous pteropods collected in a deep sediment trap in the Sargasso Sea, *Deep Sea Research Part A. Oceanographic Research Papers*, 35(3), 441-464, doi:10.1016/0198-0149(88)90020-9.
- Andersson, A., N. Bates, and F. Mackenzie (2007), Dissolution of Carbonate Sediments Under Rising pCO₂ and Ocean Acidification: Observations from Devil's Hole, Bermuda, *Aquat. Geochem.*, 13(3), 237-264, doi:10.1007/s10498-007-9018-8.
- Andersson, A. J., F. T. Mackenzie, and N. R. Bates (2008), Life on the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers, *Marine Ecology Progress Series*, 373, 265-273, doi:10.3354/meps07639.
- Anthony, K. R. N., D. I. Kline, G. Diaz-Pulido, S. Dove, and O. Hoegh-Guldberg (2008), Ocean acidification causes bleaching and productivity loss in coral reef builders, *Proceedings of the National Academy of Sciences*, 105, 17442–17446, doi:10.1073/pnas.0804478105.

- Anthony, K. R. N., J. A. Kleypas, and J.-P. Gattuso (2011a), Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification, *Global Change Biology*, *17*(12), 3655-3666, doi:10.1111/j.1365-2486.2011.02510.x.
- Anthony, K. R. N., J. A. Maynard, G. Diaz-Pulido, P. J. Mumby, P. A. Marshall, L. Cao, and O. Hoegh-Guldberg (2011b), Ocean acidification and warming will lower coral reef resilience, *Global Change Biology*, *17*(5), 1798–1808, doi:10.1111/j.1365-2486.2010.02364.x.
- Archer, D., and E. Maier-Reimer (1994), Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration, *Nature*, *367*(6460), 260-263, doi:10.1038/367260a0.
- Archer, D. (1996), A data-driven model of the global calcite lysocline, *Global Biogeochem. Cycles*, *10*(3), 511-526
- Archer, D., M. Eby, V. Brovkin, A. Ridgwell, L. Cao, U. Mikolajewicz, K. Caldeira, K. Matsumoto, G. Munhoven, A. Montenegro, and K. Tokos (2009), Atmospheric Lifetime of Fossil Fuel Carbon Dioxide, *Annual Review of Earth and Planetary Sciences*, 37(1), 117-134, doi:10.1146/annurev.earth.031208.100206.
- Balch, W. M., D. T. Drapeau, B. C. Bowler, E. Lyczskowski, E. S. Booth, and D. Alley (2011), The contribution of coccolithophores to the optical and inorganic carbon budgets during the Southern Ocean Gas Exchange Experiment: New evidence in support of the "Great Calcite Belt" hypothesis, J. Geophys. Res., 116, C00F06, doi:10.1029/2011jc006941.
- Barton, A., B. Hales, G. G. Waldbusser, C. Langdon, and R. A. Feely (2012), The Pacific oyster, *Crassostrea gigas*, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects, *Limnol. Oceanogr.*, *57*(3), 698-710
- Bathmann, U. V., T. T. Noji, and B. von Bodungen (1991), Sedimentation of pteropods in the Norwegian Sea in autumn, *Deep Sea Research Part A*. *Oceanographic Research Papers*, 38(10), 1341-1360, doi:10.1016/0198-0149(91)90031-A.
- Bednarsek, N., G. A. Tarling, S. Fielding, and D. C. E. Bakker (2012), Population dynamics and biogeochemical significance of *Limacina helicina antarctica* in the Scotia Sea (Southern Ocean), *Deep Sea Res. Part II, Volumes 59–60*, 105–116, doi:10.1016/j.dsr2.2011.08.003.
- Berger, W. H. (1970), Biogenous deep-sea sediments: Fractionation by deep-sea circulation, *Geol. Soc. Am. Bull.*, *81*, 1385-1401, doi:10.1130/0016-7606(1970) 81[1385:BDSFBD]2.0.CO;2.
- Bijma, J., B. Hönisch, and R. E. Zeebe (2002), Impact of ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W.S. Broecker and E. Clark, *Geochemistry Geophysics Geosystems*, 11(3), 1064, doi:10.1029/2002GC000388.
- Bostock, H. C., B. W. Hayward, H. L. Neil, K. I. Currie, and G. B. Dunbar (2011), Deep-water carbonate concentrations in the southwest Pacific, *Deep Sea Res. Part I*, *58*(1), 72-85, doi:10.1016/j.dsr.2010.11.010.
- Bowler, C., D. M. Karl, and R. R. Colwell (2009), Microbial oceanography in a sea of opportunity, *Nature*, 459(7244), 180-184, doi:10.1038/nature08056.
- Brewer, P. G., and E. T. Peltzer (2009), Limits to Marine Life, *Science*, *324*(5925), 347-348, doi:10.1126/science.1170756.

- Brierley, A. S., and M. J. Kingsford (2009), Impacts of Climate Change on Marine Organisms and Ecosystems, *Current Biology*, 19(14), R602-R614, doi:10.1016/j.cub.2009.05.046.
- Byrne, M. (2010), Impact of climate change stressors on marine invertebrate life histories with a focus on the Mollusca and Echinodermata, in *Climate alert: Climate change monitoring and strategy*, edited by J. Yu and A. Henderson-Sellers, pp. 142-185, University of Sydney Press, Sydney.
- Byrne, M. (2011), Impact of ocean warming and ocean acidification on marine invertebrate life history stages: vulnerabilities and potential for persistence in a changing ocean, *Oceanography and Marine Biology: An Annual Review*, 49, 1-42
- Byrne, M., M. Ho, E. Wong, N. A. Soars, P. Selvakumaraswamy, H. Shepard-Brennand, S. A. Dworjanyn, and A. R. Davis (2011), Unshelled abalone and corrupted urchins: development of marine calcifiers in a changing ocean, *Proceedings of the Royal Society B: Biological Sciences*, 278(1716), 2376-2383, doi:10.1098/rspb.2010.2404.
- Byrne, M. (2012), Global change ecotoxicology: Identification of early life history bottlenecks in marine invertebrates, variable species responses and variable experimental approaches, *Marine Environmental Research*, *76*, 3-15, doi:10.1016/j.marenvres.2011.10.004.
- Byrne, R. H., and W. Yao (2008), Procedures for measurement of carbonate ion concentrations in seawater by direct spectrophotometric observations of Pb(II) complexation, *Mar. Chem.*, *112*(1-2), 128-135, doi:10.1016/j.marchem.2008.07.009.
- Byrne, R. H., S. Mecking, R. A. Feely, and X. Liu (2010), Direct observations of basin-wide acidification of the North Pacific Ocean, *Geophys. Res. Lett.*, *37*(2), L02601, doi:10.1029/2009gl040999.
- Chan, K. Y. K., D. Grünbaum, and M. J. O'Donnell (2011), Effects of oceanacidification-induced morphological changes on larval swimming and feeding, *The Journal of Experimental Biology*, 214(22), 3857-3867, doi:10.1242/jeb.054809.
- Chave, K. E. (1954), Aspects of the Biogeochemistry of Magnesium 1. Calcareous Marine Organisms, *J. Geol.*, *62*(3), 266-283, doi:10.1086/626162.
- Checkley, D. M., Jr., A. G. Dickson, M. Takahashi, J. A. Radich, N. Eisenkolb, and R. Asch (2009), Elevated CO₂ Enhances Otolith Growth in Young Fish, *Science*, *324*(5935), 1683, doi:10.1126/science.1169806.
- Christensen, A. B., H. D. Nguyen, and M. Byrne (2011), Thermotolerance and the effects of hypercapnia on the metabolic rate of the ophiuroid *Ophionereis schayeri*: Inferences for survivorship in a changing ocean, *Journal of Experimental Marine Biology and Ecology*, 403(1-2), 31-38, doi:10.1016/j.jembe.2011.04.002.
- Coen, L. D., M. W. Luckenbacj, and D. L. Breitberg (1999), The role of oyster beds as an essential fish habitat: a review of current knowledge and some new perspectives, *Estuaries*, *25*, 1323-1354
- Collins, S., and G. Bell (2004), Phenotypic consequences of 1,000 generations of selection at elevated CO₂ in a green alga, *Nature*, *431*(7008), 566-569
- Comeau, S., G. Gorsky, R. Jeffree, J. L. Teyssié, and J. P. Gattuso (2009), Impact of ocean acidification on a key Arctic pelagic mollusc (*Limacina helicina*), *Biogeosciences*, 6(9), 1877-1882
- Cooley, S. R., and S. C. Doney (2009), Anticipating ocean acidification's economic consequences for commercial fisheries, *Environmental Research Letters*, 4, 024007, doi:10.1088/1748-9326/4/2/024007.

- Cooley, S. R., H. Kite-Powell, and S. C. Doney (2009), Ocean Acidification's Potential to Alter Global Marine Ecosystem Services, *Oceanography*, 22(4), 172-181
- Cooper, T. F., G. De'Ath, K. E. Fabricius, and J. M. Lough (2008), Declining coral calcification in massive *Porites* in two nearshore regions of the northern Great Barrier Reef, *Global Change Biology*, *14*, 529-538, doi:10.1111/j.1365-2486.2007.01520.x.
- Cooper, T. F., R. A. O'Leary, and J. M. Lough (2012), Growth of Western Australian Corals in the Anthropocene, *Science*, *335*(6068), 593-596, doi:10.1126/science.1214570.
- Crowley, T. J. (1983), Calcium-carbonate preservation patterns in the Central North Atlantic during the last 150,000 years, *Mar. Geol.*, *51*, 1-14
- Cubillos, J. C., S. W. Wright, G. Nash, M. F. de Salas, B. Griffiths, B. Tilbrook, A. Poisson, and G. M. Hallegraeff (2007), Calcification morphotypes of the coccolithophorid *Emiliania huxleyi* in the Southern Ocean: changes in 2001 to 2006 compared to historical data, *Marine Ecology Progress Series*, *348*, 47-54, doi:10.3354/meps07058.
- Cummings, V., J. Hewitt, A. Van Rooyen, K. Currie, S. Beard, S. Thrush, J. Norkko, N. Barr, P. Heath, N. J. Halliday, R. Sedcole, A. Gomez, C. McGraw, and V. Metcalf (2011), Ocean Acidification at High Latitudes: Potential Effects on Functioning of the Antarctic Bivalve *Laternula elliptica*, *PLoS ONE*, 6(1), e16069, doi:10.1371/journal.pone.0016069.
- de Moel, H., G. M. Ganssen, F. J. C. Peeters, S. J. A. Jung, D. Kroon, G. J. A. Brummer, and R. E. Zeebe (2009), Planktic foraminiferal shell thinning in the Arabian Sea due to anthropogenic ocean acidification?, *Biogeosciences*, 6(9), 1917-1925
- De'ath, G., J. M. Lough, and K. E. Fabricius (2009), Declining Coral Calcification on the Great Barrier Reef, *Science*, *323*(5910), 116-119, doi:10.1126/science.1165283.
- DeVries, T., and F. Primeau (2009), Atmospheric pCO₂ sensitivity to the solubility pump: Role of the low-latitude ocean, *Global Biogeochem. Cycles*, *23*, GB4020, doi:10.1029/2009gb003537.
- Dias, B. B., M. B. Hart, C. W. Smart, and J. M. Hall-Spencer (2010), Modern seawater acidification: the response of foraminifera to high-CO₂ conditions in the Mediterranean Sea, *J. Geol. Soc.*, *167*(5), 843-846, doi:10.1144/0016-76492010-050.
- Diaz-Pulido, G., M. Gouezo, B. Tilbrook, S. Dove, and K. R. N. Anthony (2011), High CO₂ enhances the competitive strength of seaweeds over corals, *Ecology Letters*, 14(2), 156-162, doi:10.1111/j.1461-0248.2010.01565.x.
- Diaz-Pulido, G., K. R. N. Anthony, D. I. Kline, S. Dove, and O. Hoegh-Guldberg (2012), Interactions between ocean acidification and warming on the mortality and dissolution of coralline algae, *Journal Of Phycology*, *48*(1), 32-39, doi:10.1111/j.1529-8817.2011.01084.x.
- Dissard, D., G. Nehrke, G. J. Reichart, and J. Bijma (2010), Impact of seawater pCO₂ on calcification and Mg/Ca and Sr/Ca ratios in benthic foraminifera calcite: results from culturing experiments with *Ammonia tepida*, *Biogeosciences*, 7(1), 81-93
- Dixson, D. L., P. L. Munday, and G. P. Jones (2010), Ocean acidification disrupts the innate ability of fish to detect predator olfactory cues, *Ecology Letters*, *13*(1), 68-75, doi:10.1111/j.1461-0248.2009.01400.x.

- Domenici, P., B. Allan, M. I. McCormick, and P. L. Munday (2012), Elevated carbon dioxide affects behavioural lateralization in a coral reef fish, *Biology Letters*, 8(1), 78-81, doi:10.1098/rsbl.2011.0591.
- Doney, S. C., V. J. Fabry, R. A. Feely, and J. A. Kleypas (2009), Ocean Acidification: The Other CO₂ Problem, *Annual Review of Marine Science*, 1(1), 169-192, doi:10.1146/annurev.marine.010908.163834.
- Doney, S. C. (2010), The Growing Human Footprint on Coastal and Open-Ocean Biogeochemistry, *Science*, *328*(5985), 1512-1516, doi:10.1126/science.1185198.
- Dupont, S., O. Ortega-Martínez, and M. Thorndyke (2010), Impact of near-future ocean acidification on echinoderms, *Ecotoxicology*, *19*(3), 449-462, doi:10.1007/s10646-010-0463-6.
- Durack, P. J., S. E. Wijffels, and R. J. Matear (2012), Ocean Salinities Reveal Strong Global Water Cycle Intensification During 1950 to 2000, *Science*, *336*(6080), 455-458, doi:10.1126/science.1212222.
- Erez, J., S. Reynaud, J. Silverman, K. Schneider, and D. Allemand (2011), Coral Calcification Under Ocean Acidification and Global Change
- Coral Reefs: An Ecosystem in Transition, edited by Z. Dubinsky and N. Stambler, pp. 151-176, Springer Netherlands.
- Ericson, J., M. Ho, A. Miskelly, C. King, P. Virtue, B. Tilbrook, and M. Byrne (2012), Combined effects of two ocean change stressors, warming and acidification, on fertilization and early development of the Antarctic echinoid *Sterechinus neumayeri*, *Polar Biology*, 1-8, doi:10.1007/s00300-011-1150-7.
- Fabricius, K. E., C. Langdon, S. Uthicke, C. Humphrey, S. Noonan, G. De'ath, R. Okazaki, N. Muehllehner, M. S. Glas, and J. M. Lough (2011), Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations, *Nature Clim. Change*, 1(3), 165-169, doi:10.1038/nclimate1122.
- Fabry, V. J., and W. G. Deuser (1992), Seasonal Changes in the Isotopic Compositions and Sinking Fluxes of Euthecosomatous Pteropod Shells in the Sargasso Sea, *Paleoceanography*, 7(2), 195–213
- Fabry, V. J. (2008), Marine Calcifiers in a High-CO₂ Ocean, *Science*, *320*(5879), 1020-1022, doi:10.1126/science.1157130.
- Fabry, V. J., B. A. Seibel, R. A. Feely, and J. C. Orr (2008), Impacts of ocean acidification on marine fauna and ecosystem processes, *ICES Journal of Marine Science*, 65(3), 414-432, doi:10.1093/icesjms/fsn048.
- Farrell, J. W., and W. L. Prell (1989), Climatic change and CaCO₃ preservation: An 800,000-year bathymetric reconstruction from the central Equatorial Pacific Ocean, *Paleoceanography*, 4(4), 447-466
- Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero (2004), Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans, *Science*, 305, 362-366, doi:10.1126/science.1097329.
- Feely, R. A., S. C. Doney, and S. R. Cooley (2009), Ocean Acidification, Oceanography, 22(4), 36-47
- Feely, R. A., C. L. Sabine, R. H. Byrne, F. J. Millero, A. G. Dickson, R. Wanninkhof, A. Murata, L. A. Miller, and D. Greeley (2012), Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean, *Global Biogeochem. Cycles*, 26(3), GB3001, doi:10.1029/2011gb004157.
- Ferrari, M. C. O., D. L. Dixson, P. L. Munday, M. I. McCormick, M. G. Meekan, A. Sih, and D. P. Chivers (2011), Intrageneric variation in antipredator responses of coral reef fishes affected by ocean acidification: implications for climate change

projections on marine communities, *Global Change Biology*, *17*(9), 2980-2986, doi:10.1111/j.1365-2486.2011.02439.x.

- Form, A. U., and U. Riebesell (2012), Acclimation to ocean acidification during longterm CO₂ exposure in the cold-water coral *Lophelia pertusa*, *Global Change Biology*, *18*(3), 843-853, doi:10.1111/j.1365-2486.2011.02583.x.
- Foster, G. L. (2008), Seawater pH, pCO₂ and [CO₃²⁻] variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera, *Earth Planet. Sci. Lett.*, 271(1-4), 254-266, doi:<u>10.1016/j.epsl.2008.04.015</u>.
- Fransson, A., M. Chierici, P. L. Yager, and W. O. Smith, Jr. (2011), Antarctic sea ice carbon dioxide system and controls, J. Geophys. Res., 116(C12), C12035, doi:10.1029/2010jc006844.
- Friedrich, T., A. Timmermann, A. Abe-Ouchi, N. R. Bates, M. O. Chikamoto, M. J. Church, J. E. Dore, D. K. Gledhill, M. Gonzalez-Davila, M. Heinemann, T. Ilyina, J. H. Jungclaus, E. McLeod, A. Mouchet, and J. M. Santana-Casiano (2012), Detecting regional anthropogenic trends in ocean acidification against natural variability, *Nature Clim. Change*, 2, 167–171, doi:10.1038/nclimate1372.
- Gattuso, J.-P., J. Bijma, M. Gehlen, U. Riebesell, and C. Turley (2011), Ocean Acidification: knowns, unknowns and perspectives, in *Ocean Acidification*, edited by J.-P. Gattuso and L. Hansson, pp. 291- 309, Oxford University Press, New York.
- Gattuso, J. P., M. Frankignoulle, I. Bourge, S. Romaine, and R. W. Buddemeier (1998), Effect of calcium carbonate saturation of seawater on coral calcification, *Global Planet. Change*, *18*(1,Äì2), 37-46, doi:10.1016/s0921-8181(98)00035-6.
- Gazeau, F., J. M. Jansen, J.-P. Gattuso, J. J. Middelburg, and C. H. R. Heip (2007), Impact of elevated CO₂ on shellfish calcification, *Geophys. Res. Lett.*, *34*, L07603, doi:10.1029/2006GL028554.
- Gazeau, F., J. P. Gattuso, C. Dawber, A. E. Pronker, F. Peene, J. Peene, C. H. R. Heip, and J. J. Middelburg (2010), Effect of ocean acidification on the early life stages of the blue mussel *Mytilus edulis*, *Biogeosciences*, 7(7), 2051-2060, doi:10.5194/bg-7-2051-2010.
- González-Dávila, M., J. M. Santana-Casiano, M. J. Rueda, and O. Llinás (2010), The water column distribution of carbonate system variables at the ESTOC site from 1995 to 2004, *Biogeosciences*, 7(10), 3067-3081, doi:10.5194/bg-7-3067-2010.
- Gooday, A. J., and F. J. Jorissen (2011), Benthic Foraminiferal Biogeography:
 Controls on Global Distribution Patterns in Deep-Water Settings, *Annual Review of Marine Science*, 4(1), 237-262, doi:10.1146/annurev-marine-120709-142737.
- Goodwin, P., and A. Ridgwell (2010), Ocean-atmosphere partitioning of anthropogenic carbon dioxide on multimillennial timescales, *Global Biogeochem*. *Cycles*, *24*(2), GB2014, doi:10.1029/2008gb003449.
- Gruber, N. (2011), Warming up, turning sour, losing breath: ocean biogeochemistry under global change, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *369*(1943), 1980-1996, doi:10.1098/rsta.2011.0003.
- Guinotte, J. M., J. Orr, S. Cairns, A. Freiwald, L. Morgan, and R. George (2006), Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals?, *Frontiers in Ecology and Environment*, 4(3), 141-146
- Hall-Spencer, J. M., R. Rodolfo-Metalpa, S. Martin, E. Ransome, M. Fine, S. M. Turner, S. J. Rowley, D. Tedesco, and M.-C. Buia (2008), Volcanic carbon dioxide vents show ecosystem effects of ocean acidification, *Nature*, 454, 96-99, doi:10.1038/nature07051.

- Hallock, P. (2005), Global change and modern coral reefs: New opportunities to understand shallow-water carbonate depositional processes, *Sediment. Geol.*, *175*(1-4), 19-33, doi:10.1016/j.sedgeo.2004.12.027.
- Havenhand, J. N., F.-R. Buttler, M. C. Thorndyke, and J. E. Williamson (2008), Nearfuture levels of ocean acidification reduce fertilization success in a sea urchin, *Current Biology*, 18(15), R651-R652, doi:10.1016/j.cub.2008.06.015.
- Havenhand, J. N., and P. Schlegel (2009), Near-future levels of ocean acidification do not affect sperm motility and fertilization kinetics in the oyster *Crassostrea gigas*, *Biogeosciences*, 6(12), 3009-3015, doi:10.5194/bg-6-3009-2009.
- Hobday, A. J., and J. M. Lough (2011), Projected climate change in Australian marine and freshwater environments, *Marine and Freshwater Research*, 62(9), 1000-1014, doi:10.1071/MF10302.

Hodell, D. A., C. D. Charles, and F. J. Sierro (2001), Late Pleistocene evolution of the ocean's carbonate system, *Earth Planet. Sci. Lett.*, 192, 109-124

- Hoegh-Guldberg, O. (2005), Low coral cover in a high-CO₂ world, J. Geophys. Res., 110, C09S06, doi:10.1029/2004JC002528.
- Hoegh-Guldberg, O., P. J. Mumby, A. J. Hooten, R. S. Steneck, P. Greenfield, E. Gomez, C. D. Harvell, P. F. Sale, A. J. Edwards, K. Caldeira, N. Knowlton, C. M. Eakin, R. Iglesias-Prieto, N. Muthiga, R. H. Bradbury, A. Dubi, and M. E. Hatziolos (2007), Coral Reefs Under Rapid Climate Change and Ocean Acidification, *Science*, *318*(5857), 1737-1742, doi:10.1126/science.1152509.
- Hofmann, G. E., J. E. Smith, K. S. Johnson, U. Send, L. A. Levin, F. Micheli, A. Paytan, N. N. Price, B. Peterson, Y. Takeshita, P. G. Matson, E. D. Crook, K. J. Kroeker, M. C. Gambi, E. B. Rivest, C. A. Frieder, P. C. Yu, and T. R. Martz (2011), High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem Comparison, *PLoS ONE*, 6(12), e28983
- Hong, G.-H., and C.-T. A. Chen (2002), Aragonitic Pteropod Flux to the Interior of the East Sea (Sea of Japan), *TAO*, *13*(2), 205-210
- Hönisch, B., and N. G. Hemming (2005), Surface ocean pH response to variation in pCO₂ through two full glacial cycles, *Earth Planet. Sci. Lett.*, 236, 305-314, doi:10.1016/j.epsl.2005.04.027.
- Hönisch, B., N. G. Hemming, D. Archer, M. Siddall, and J. F. McManus (2009), Atmospheric Carbon Dioxide Concentration Across the Mid-Pleistocene Transition, *Science*, 324(5934), 1551-1554, doi:10.1126/science.1171477.
- Hönisch, B., A. Ridgwell, D. N. Schmidt, E. Thomas, S. J. Gibbs, A. Sluijs, R. Zeebe, L. Kump, R. C. Martindale, S. E. Greene, W. Kiessling, J. Ries, J. C. Zachos, D. L. Royer, S. Barker, T. M. Marchitto, R. Moyer, C. Pelejero, P. Ziveri, G. L. Foster, and B. Williams (2012), The Geological Record of Ocean Acidification, *Science*, 335(6072), 1058-1063, doi:10.1126/science.1208277.
- Honjo, S., S. J. Manganini, R. A. Krishfield, and R. Francois (2008), Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983, *Prog. Oceanogr.*, 76(3), 217-285, doi:10.1016/j.pocean.2007.11.003.
- Hood, R. R., E. A. Laws, R. A. Armstrong, N. R. Bates, C. W. Brown, C. A. Carlson, F. Chai, S. C. Doney, P. G. Falkowski, R. A. Feely, M. A. M. Friedrichs, M. R. Landry, J. Keith Moore, D. M. Nelson, T. L. Richardson, B. Salihoglu, M. Schartau, D. A. Toole, and J. D. Wiggert (2006), Pelagic functional group modeling: Progress, challenges and prospects, *Deep Sea Res. Part II*, 53(5-7), 459-512, doi:10.1016/j.dsr2.2006.01.025.

- Howard, W. R., and W. L. Prell (1994), Late Quaternary carbonate production and preservation in the Southern Ocean: Implications for oceanic and atmospheric carbon cycling, *Paleoceanography*, *9*(3), 453-482, doi:10.1029/93PA03524.
- Howard, W. R., D. Roberts, A. D. Moy, M. C. M. Lindsay, R. R. Hopcroft, T. W. Trull, and S. G. Bray (2011), Distribution, abundance and seasonal flux of pteropods in the Sub-Antarctic Zone, *Deep Sea Res. Part II*, 58, 2293-2300, doi:10.1016/j.dsr2.2011.05.031.
- Hughen, K., S. Lehman, J. Southon, J. T. Overpeck, O. Marchal, C. Herring, and J. Turnbull (2004), ¹⁴C activity and global carbon cycle changes over the past 50,000 years, *Science*, *303*, 202-207
- Hughes, T. P., N. A. J. Graham, J. B. C. Jackson, P. J. Mumby, and R. S. Steneck (2010), Rising to the challenge of sustaining coral reef resilience, *Trends in Ecology & Evolution*, 25(11), 633-642, doi:10.1016/j.tree.2010.07.011.
- Hunt, B. P. V., E. A. Pakhomov, G. W. Hosie, V. Siegel, P. Ward, and K. Bernard (2008), Pteropods in Southern Ocean ecosystems, *Prog. Oceanogr.*, 78(3), 193-221, doi:10.1016/j.pocean.2008.06.001.
- Hutchins, D. A., M. R. Mulholland, and F. Fu (2009), Nutrient cycles and marine microbes in a CO₂-enriched ocean, *Oceanography*, 22(4), 128–145, doi:10.5670/oceanog.2009.103.
- Iglesias-Rodriguez, M. D., R. Armstrong, R. A. Feely, R. Hood, J. Kleypas, J. D. Milliman, C. L. Sabine, and J. Sarmiento (2002), Progress made in study of ocean's calcium carbonate budget, *EOS Transactions of the American Geophysical Union*, 83(34), 365-375
- Iglesias-Rodriguez, M. D., P. R. Halloran, R. E. M. Rickaby, I. R. Hall, E. Colmenero-Hidalgo, J. R. Gittins, D. R. H. Green, T. Tyrrell, S. J. Gibbs, P. von Dassow, E. Rehm, E. V. Armbrust, and K. P. Boessenkool (2008), Phytoplankton Calcification in a High-CO₂ World, *Science*, *320*(5874), 336-340, doi:10.1126/science.1154122.
- Ilyina, T., R. E. Zeebe, E. Maier-Reimer, and C. Heinze (2009), Early detection of ocean acidification effects on marine calcification, *Global Biogeochem. Cycles*, 23, GB1008, doi:10.1029/2008GB003278.
- Jasper, J. P., and W. G. Deuser (1993), Annual cycles of mass flux and isotopic composition of pteropod shells settling into the deep Sargasso Sea, *Deep Sea Res.*, 40(4), 653-669, doi:10.1016/0967-0637(93)90064-A.
- Jin, X., N. Gruber, J. P. Dunne, J. L. Sarmiento, and R. A. Armstrong (2006), Diagnosing the contribution of phytoplankton functional groups to the production and export of particulate organic carbon, CaCO₃, and opal from global nutrient and alkalinity distributions, *Global Biogeochem. Cycles*, 20, GB2015, doi:10.1029/2005GB002532.
- Johnson, V. R., B. D. Russell, K. E. Fabricius, C. Brownlee, and J. M. Hall-Spencer (2012), Temperate and tropical brown macroalgae thrive, despite decalcification, along natural CO₂ gradients, *Global Change Biology*, doi:10.1111/j.1365-2486.2012.02716.x.
- Joint, I., S. C. Doney, and D. M. Karl (2011), Will ocean acidification affect marine microbes?, *ISME Journal of Microbial Ecology*, 5(1), 1-7, doi:10.1038/ismej.2010.79.
- Jury, C. P., R. F. Whitehead, and A. M. Szmant (2010), Effects of variations in carbonate chemistry on the calcification rates of *Madracis auretenra* (= *Madracis mirabilis* sensu Wells, 1973): bicarbonate concentrations best predict calcification

rates, *Global Change Biology*, *16*(5), 1632-1644, doi:10.1111/j.1365-2486.2009.02057.x.

- Kawaguchi, S., H. Kurihara, R. King, L. Hale, T. Berli, J. P. Robinson, A. Ishida, M. Wakita, P. Virtue, S. Nicol, and A. Ishimatsu (2010), Will krill fare well under Southern Ocean acidification?, *Biology Letters*, 7(2), 288-291, doi:10.1098/rsbl.2010.0777.
- Kheshgi, H. (1995), Sequestering atmospheric carbon dioxide by increasing ocean alkalinity, *Energy*, 20(9), 915-922, doi:10.1016/0360-5442(95)00035-F.
- Kleypas, J., R. Buddemeier, D. Archer, J. Gattuso, C. Langdon, and B. Opdyke (1999), Geochemical consequences of increased atmospheric carbon dioxide on coral reefs, *Science*, 284, 118-120
- Kleypas, J. A., K. R. N. Anthony, and J.-P. Gattuso (2011), Coral Reefs Modify Their Seawater Carbon Chemistry – Case Study from a Barrier Reef (Moorea, French Polynesia), *Global Change Biology*, 17(12), 3667–3678, doi:10.1111/j.1365-2486.2011.02530.x.
- Kline, D. I., L. Teneva, K. Schneider, T. Miard, A. Chai, M. Marker, K. Headley, B. Opdyke, M. Nash, M. Valetich, J. K. Caves, B. D. Russell, S. D. Connell, B. J. Kirkwood, P. Brewer, E. Peltzer, J. Silverman, K. Caldeira, R. B. Dunbar, J. R. Koseff, S. G. Monismith, B. G. Mitchell, S. Dove, and O. Hoegh-Guldberg (2012), A short-term in situ CO₂ enrichment experiment on Heron Island (GBR), *Sci. Rep.*, 2, doi:10.1038/srep00413.
- Kroeker, K. J., R. L. Kordas, R. N. Crim, and G. G. Singh (2010), Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms, *Ecology Letters*, *13*(11), 1419-1434, doi:10.1111/j.1461-0248.2010.01518.x.
- Kuffner, I. B., A. J. Andersson, P. L. Jokiel, K. S. Rodgers, and F. T. Mackenzie (2007), Decreased abundance of crustose coralline algae due to ocean acidification, *Nat. Geosci.*, 1, 114 - 117, doi:10.1038/ngeo100.
- Kurihara, H. (2008), Effects of CO₂-driven ocean acidification on the early developmental stages of invertebrates, *Marine Ecology Progress Series*, 373, 275-284, doi:<u>10.3354/meps07802</u>.
- Kuroyanagi, A., H. Kawahata, A. Suzuki, K. Fujita, and T. Irie (2009), Impacts of ocean acidification on large benthic foraminifers: Results from laboratory experiments, *Mar. Micropaleontol.*, 73(3-4), 190-195, doi:10.1016/j.marmicro.2009.09.003.
- Langdon, C., and M. J. Atkinson (2005), Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment, *J. Geophys. Res.*, *110*, C09S07, doi:10.1029/2004JC002576.
- Langenbuch, M., and H. O. Pörtner (2003), Energy budget of hepatocytes from Antarctic fish (*Pachycara brachycephalum* and *Lepidonotothen kempi*) as a function of ambient CO₂: pH-dependent limitations of cellular protein biosynthesis?, *Journal of Experimental Biology*, 206(22), 3895-3903, doi:10.1242/jeb.00620.
- Law, C. S., E. Breitbarth, L. J. Hoffmann, C. M. McGraw, R. J. Langlois, J. LaRoche, A. Marriner, and K. A. Safi (2012), No stimulation of nitrogen fixation by nonfilamentous diazotrophs under elevated CO₂ in the South Pacific, *Global Change Biology*, doi:10.1111/j.1365-2486.2012.02777.x.
- Le Quéré, C., M. R. Raupach, J. G. Canadell, G. Marland, L. Bopp, P. Ciais, T. J. Conway, S. C. Doney, R. A. Feely, P. Foster, P. Friedlingstein, K. Gurney, R. A. Houghton, J. I. House, C. Huntingford, P. E. Levy, M. R. Lomas, J. Majkut, N.

Metzl, J. P. Ometto, G. P. Peters, I. C. Prentice, J. T. Randerson, S. W. Running, J. L. Sarmiento, U. Schuster, S. Sitch, T. Takahashi, N. Viovy, G. R. van der Werf, and F. I. Woodward (2009), Trends in the sources and sinks of carbon dioxide, *Nat. Geosci.*, *2*, 831-836, doi:10.1038/ngeo689.

- LeBrasseur, R. J. (1966), Stomach Contents of Salmon and Steelhead Trout in the Northeastern Pacific Ocean, *Journal of the Fisheries Research Board of Canada*, 23(1), 85-100, doi:10.1139/f66-007.
- Lefebvre, S. C., I. Benner, J. H. Stillman, A. E. Parker, M. K. Drake, P. E. Rossignol, K. M. Okimura, T. Komada, and E. J. Carpenter (2011), Nitrogen source and pCO₂ synergistically affect carbon allocation, growth and morphology of the coccolithophore *Emiliania huxleyi*: potential implications of ocean acidification for the carbon cycle, *Global Change Biology*, 18(2), 493–503, doi:10.1111/j.1365-2486.2011.02575.x.
- Leon-Rodriguez, L., and G. R. Dickens (2010), Constraints on ocean acidification associated with rapid and massive carbon injections: The early Paleogene record at ocean drilling program site 1215, equatorial Pacific Ocean, *Palaeogeography*, *Palaeoclimatology*, *Palaeoecology*, 298(3-4), 409-420, doi:10.1016/j.palaeo.2010.10.029.
- Lohbeck, K. T., U. Riebesell, and T. B. H. Reusch (2012), Adaptive evolution of a key phytoplankton species to ocean acidification, *Nature Geosci*, 5, 346–351, doi:10.1038/ngeo1441.
- Lombard, F., R. E. da Rocha, J. Bijma, and J. P. Gattuso (2010), Effect of carbonate ion concentration and irradiance on calcification in planktonic foraminifera, *Biogeosciences*, 7(1), 247-255
- Lough, J. M., and T. F. Cooper (2011), New insights from coral growth band studies in an era of rapid environmental change, *Earth-Science Reviews*, *108*(3-4), 170-184, doi:10.1016/j.earscirev.2011.07.001.
- Lough, J. M., and A. J. Hobday (2011), Observed climate change in Australian marine and freshwater environments, *Marine and Freshwater Research*, 62(9), 984-999, doi:10.1071/MF10272.
- Lüthi, D., M. Le Floch, B. Bereiter, T. Blunier, J.-M. Barnola, U. Siegenthaler, D. Raynaud, J. Jouzel, H. Fischer, K. Kawamura, and T. F. Stocker (2008), High-resolution carbon dioxide concentration record 650,000-800,000 years before present, *Nature*, 453(7193), 379-382, doi:10.1038/nature06949.
- Maier, C., J. Hegeman, M. G. Weinbauer, and J. P. Gattuso (2009), Calcification of the cold-water coral *Lophelia pertusa*, under ambient and reduced pH, *Biogeosciences*, 6(8), 1671-1680
- Manzello, D. P., J. A. Kleypas, D. A. Budd, C. M. Eakin, P. W. Glynn, and C. Langdon (2008), Poorly cemented coral reefs of the eastern tropical Pacific: Possible insights into reef development in a high-CO₂ world, *Proceedings of the National Academy of Sciences*, *105*(30), 10450-10455, doi:10.1073/pnas.0712167105.
- Marchitto, T. M., J. Lynch-Stieglitz, and S. R. Hemming (2005), Deep Pacific CaCO₃ compensation and glacial-interglacial atmospheric CO₂, *Earth Planet. Sci. Lett.*, *231*(3-4), 317-336, doi:10.1016/j.epsl.2004.12.024.
- Martin, S., R. Rodolfo-Metalpa, E. Ransome, S. Rowley, M.-C. Buia, J.-P. Gattuso, and J. Hall-Spencer (2008), Effects of naturally acidified seawater on seagrass calcareous epibionts, *Biology Letters*, *4*(6), 689-692, doi:10.1098/rsbl.2008.0412.

Martin, S., and J.-P. Gattuso (2009), Response of Mediterranean coralline algae to ocean acidification and elevated temperature, *Global Change Biology*, *15*(8), 2089-2100, doi:10.1111/j.1365-2486.2009.01874.x.

Martin, S., S. Richier, M.-L. Pedrotti, S. Dupont, C. Castejon, Y. Gerakis, M.-E. Kerros, F. Oberhänsli, J.-L. Teyssié, R. Jeffree, and J.-P. Gattuso (2011), Early development and molecular plasticity in the Mediterranean sea urchin *Paracentrotus lividus* exposed to CO₂-driven acidification, *The Journal of Experimental Biology*, 214(8), 1357-1368, doi:10.1242/jeb.051169.

Martz, T. R., H. W. Jannasch, and K. S. Johnson (2009), Determination of carbonate ion concentration and inner sphere carbonate ion pairs in seawater by ultraviolet spectrophotometric titration, *Mar. Chem.*, 115(3-4), 145-154, doi:10.1016/j.marchem.2009.07.002.

Marubini, F., and B. Thake (1999), Bicarbonate addition promotes coral growth, *Limnol. Oceanogr.*, 44(3), 716-720

- Matear, R. J., and B. I. McNeil (2003), Decadal accumulation of anthropogenic CO₂ in the Southern Ocean: A comparison of CFC-age derived estimates to multiplelinear regression estimates, *Global Biogeochemical Cycles*, *17*(4), 1113, doi:10.1029/2003GB002089.
- Matear, R. J., and A. Lenton (2008), Impact of Historical Climate Change on the Southern Ocean Carbon Cycle, *Journal of Climate*, *21*, 5820–5834, doi:10.1175/2008JCLI2194.1.

Matthews, H. D., L. Cao, and K. Caldeira (2009), Sensitivity of ocean acidification to geoengineered climate stabilization, *Geophysical Ressearch Letters*, *36*, doi:10.1029/2009GL037488.

McClintock, J. B., R. A. Angus, M. R. McDonald, C. D. Amsler, S. A. Catledge, and Y. K. Vohra (2009), Rapid dissolution of shells of weakly calcified Antarctic benthic macroorganisms indicates high vulnerability to ocean acidification, *Antarctic Science*, 21(05), 449-456, doi:doi:10.1017/S0954102009990198.

McCulloch, M., J. Falter, J. Trotter, and P. Montagna (2012a), Coral resilience to ocean acidification and global warming through pH up-regulation, *Nature Clim. Change, advance online publication*, doi:10.1038/nclimate1473.

McCulloch, M., J. Trotter, P. Montagna, J. Falter, R. Dunbar, A. Freiwald, G.
Försterra, M. López Correa, C. Maier, A. Rüggeberg, and M. Taviani (2012b),
Resilience of cold-water scleractinian corals to ocean acidification: Boron isotopic systematics of pH and saturation state up-regulation, *Geochim. Cosmochim. Acta*, 87, 21-34, doi:10.1016/j.gca.2012.03.027.

- McElroy, D. J., H. D. Nguyen, and M. Byrne (2012), Respiratory response of the intertidal seastar *Parvulastra exigua* to contemporary and near-future pulses of warming and hypercapnia, *Journal of Experimental Marine Biology and Ecology*, 416-417, 1-7, doi:10.1016/j.jembe.2012.02.003.
- McNeil, B. I., N. Metzl, R. M. Key, R. J. Matear, and A. Corbiere (2007), An empirical estimate of the Southern Ocean air-sea CO₂ flux, *Global Biogeochemical Cycles*, *21*, GB3011, doi:10.1029/2007GB002991.
- McNeil, B. I., and R. J. Matear (2008), Southern Ocean acidification: A tipping point at 450-ppm atmospheric CO₂, *Proceedings of the National Academy of Sciences*, *105*(48), 18860–18864 doi:10.1073/pnas.0806318105.
- McNeil, B. I. (2010), Diagnosing coastal ocean CO₂ interannual variability from a 40 year hydrographic time series station off the east coast of Australia, *Global Biogeochem. Cycles*, *24*(4), GB4034, doi:10.1029/2010gb003870.

- McNeil, B. I., C. Sweeney, and J. A. E. Gibson (2011), Natural seasonal variability of aragonite saturation state within two Antarctic coastal ocean sites, *Antarctic Science*, 23, 411-412, doi:10.1017/S0954102011000204
- Meinecke, G., and G. Wefer (1990), Seasonal pteropod sedimentation in the Norwegian Sea, *Palaeogeography, Palaeoclimatology, Palaeoecology, 79*(1-2), 129-147, doi:10.1016/0031-0182(90)90109-K.
- Midorikawa, T., H. Y. Inoue, M. Ishii, D. Sasano, N. Kosugi, G. Hashida, S.-i. Nakaoka, and T. Suzuki (2012), Decreasing pH trend estimated from 35-year time series of carbonate parameters in the Pacific sector of the Southern Ocean in summer, *Deep Sea Res. Part I*, *61*, 131-139, doi:10.1016/j.dsr.2011.12.003.
- Miller, A. W., A. C. Reynolds, C. Sobrino, and G. F. Riedel (2009), Shellfish Face Uncertain Future in High CO₂ World: Influence of Acidification on Oyster Larvae Calcification and Growth in Estuaries, *PLoS ONE*, 4(5), e5661
- Mohan, R., K. Verma, L. Mergulhao, D. Sinha, S. Shanvas, and M. Guptha (2006), Seasonal variation of pteropods from the Western Arabian Sea sediment trap, *Geo-Mar. Lett.*, 26(5), 265-273, doi:10.1007/s00367-006-0035-1.
- Morse, J. W., R. S. Arvidson, and A. Lüttge (2007), Calcium Carbonate Formation and Dissolution, *Chemical Reviews*, *107*(2), 342-381, doi:10.1021/cr050358j.
- Moy, A. D., W. R. Howard, S. G. Bray, and T. W. Trull (2009), Reduced calcification in modern Southern Ocean planktonic foraminifera, *Nature Geoscience*, *2*, 276-280, doi:10.1038/ngeo460.
- Mucci, A. (1983), The solubility of calcite and aragonite in seawater at various salinities, temperatures and one atmosphere total pressure, *American Journal of Sciences*, 283, 780-799
- Müller, M. N., K. G. Schulz, and U. Riebesell (2010), Effects of long-term high CO₂ exposure on two species of coccolithophores, *Biogeosciences*, 7(3), 1109-1116, doi:10.5194/bg-7-1109-2010.
- Munday, P. L., G. P. Jones, M. S. Pratchett, and A. J. Williams (2008), Climate change and the future for coral reef fishes, *Fish and Fisheries*, *9*(3), 261-285, doi:10.1111/j.1467-2979.2008.00281.x.
- Munday, P. L., N. E. Crawley, and G. E. Nilsson (2009a), Interacting effects of elevated temperature and ocean acidification on the aerobic performance of coral reef fishes, *Marine Ecology Progress Series*, *388*, 235-242, doi:10.3354/meps08137.
- Munday, P. L., D. L. Dixson, J. M. Donelson, G. P. Jones, M. S. Pratchett, G. V. Devitsina, and K. B. Døving (2009b), Ocean acidification impairs olfactory discrimination and homing ability of a marine fish, *Proceedings of the National Academy of Sciences*, 106(6), 1848-1852 doi:10.1073/pnas.0809996106.
- Munday, P. L., J. M. Donelson, D. L. Dixson, and G. G. K. Endo (2009c), Effects of ocean acidification on the early life history of a tropical marine fish, *Proceedings* of the Royal Society B: Biological Sciences, 276(1671), 3275-3283, doi:10.1098/rspb.2009.0784.
- Munday, P. L., D. L. Dixson, M. I. McCormick, M. Meekan, M. C. O. Ferrari, and D. P. Chivers (2010), Replenishment of fish populations is threatened by ocean acidification, *Proceedings of the National Academy of Sciences*, 107 (29), 12930-12934, doi:10.1073/pnas.1004519107.
- Munday, P. L., M. Gagliano, J. M. Donelson, D. L. Dixson, and S. R. Thorrold (2011a), Ocean acidification does not affect the early life history development of a tropical marine fish, *Marine Ecology Progress Series*, 423, 211-221, doi:10.3354/meps08990.

- Munday, P. L., V. Hernaman, D. L. Dixson, and S. R. Thorrold (2011b), Effect of ocean acidification on otolith development in larvae of a tropical marine fish, *Biogeosciences*, 8(6), 1631-1641, doi:10.5194/bg-8-1631-2011.
- Nash, M. C., U. Troitzsch, B. N. Opdyke, J. M. Trafford, B. D. Russell, and D. I. Kline (2011), First discovery of dolomite and magnesite in living coralline algae and its geobiological implications, *Biogeosciences*, 8(11), 3331-3340, doi:10.5194/bg-8-3331-2011.
- Nguyen, H. D., S. S. Doo, N. A. Soars, and M. Byrne (2012), Non-calcifying larvae in a changing ocean: warming, not acidification/hypercapnia, is the dominant stressor on development of the sea star Meridiastra calcar, *Global Change Biology*, doi:10.1111/j.1365-2486.2012.02714.x.
- Opdyke, B. N., and J. C. G. Walker (1992), Return of the coral reef hypothesis: Basin to shelf partitioning of CaCO₃ and its effect on atmospheric CO₂, *Geology*, 20, 733-736
- Orr, J. C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G.-K. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M.-F. Weirig, Y. Yamanaka, and A. Yool (2005), Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, 437(7059), 681-686, doi:10.1038/nature04095.
- Pagani, M., Z. Liu, J. LaRiviere, and A. C. Ravelo (2010), High Earth-system climate sensitivity determined from Pliocene carbon dioxide concentrations, *Nature Geoscience*, 3(1), 27-30, doi:10.1038/ngeo724.
- Pandolfi, J. M., R. H. Bradbury, E. Sala, T. P. Hughes, K. A. Bjorndal, R. G. Cooke, D. McArdle, L. McClenachan, M. J. H. Newman, G. Paredes, R. R. Warner, and J. B. C. Jackson (2003), Global Trajectories of the Long-Term Decline of Coral Reef Ecosystems, *Science*, 301(5635), 955-958, doi:10.1126/science.1085706.
- Pandolfi, J. M., S. R. Connolly, D. J. Marshall, and A. L. Cohen (2011), Projecting Coral Reef Futures Under Global Warming and Ocean Acidification, *Science*, 333(6041), 418-422, doi:10.1126/science.1204794.
- Pane, L., M. Feletti, B. Francomacaro, and G. L. Mariottini (2004), Summer coastal zooplankton biomass and copepod community structure near the Italian Terra Nova Base (Terra Nova Bay, Ross Sea, Antarctica), *Journal of Plankton Research*, 26(12), 1479-1488, doi:10.1093/plankt/fbh135.
- Parker, L. M., P. M. Ross, and W. A. O'Connor (2009), The effect of ocean acidification and temperature on the fertilization and embryonic development of the Sydney rock oyster *Saccostrea glomerata* (Gould 1850), *Global Change Biology*, 15(9), 2123-2136, doi:10.1111/j.1365-2486.2009.01895.x.
- Parker, L. M., P. M. Ross, W. A. O'Connor, L. Borysko, D. A. Raftos, and H.-O. Pörtner (2012), Adult exposure influences offspring response to ocean acidification in oysters, *Global Change Biology*, 18(1), 82-92, doi:10.1111/j.1365-2486.2011.02520.x.
- Pelejero, C., E. Calvo, M. T. McCulloch, J. F. Marshall, M. K. Gagan, J. M. Lough, and B. N. Opdyke (2005), Preindustrial to modern interdecadal variability in coral reef pH, *Science*, 309(5744), 2204-2207, doi:10.1126/science.1113692.
- Pelejero, C., E. Calvo, and O. Hoegh-Guldberg (2010), Paleo-perspectives on ocean acidification
- Pilskaln, C. H., S. J. Manganini, T. W. Trull, L. Armand, W. Howard, V. L. Asper, and R. Massom (2004), Geochemical particle fluxes in the Southern Indian Ocean

seasonal ice zone: Prydz Bay region, East Antarctica, *Deep-Sea Research I*, *51*, 307-332, doi:10.1016/j.dsr.2003.10.010.

- Piontek, J., M. Lunau, N. Händel, C. Borchard, M. Wurst, and A. Engel (2010), Acidification increases microbial polysaccharide degradation in the ocean, *Biogeosciences*, 7(5), 1615-1624, doi:10.5194/bg-7-1615-2010.
- Pörtner, H.-O. (2008), Ecosystem effects of ocean acidification in times of ocean warming: a physiologist's view, *Marine Ecology Progress Series*, 373, 203-217, doi:10.3354/meps07768.
- Pörtner, H.-O. (2010), Oxygen- and capacity-limitation of thermal tolerance: a matrix for integrating climate-related stressor effects in marine ecosystems, *Journal of Experimental Biology*, 213(6), 881-893, doi:10.1242/jeb.037523.
- Pörtner, H. O., and A. P. Farrell (2008), Physiology and Climate Change, *Science*, 322(5902), 690-692, doi:10.1126/science.1163156.
- Pörtner, H. O., and M. A. Peck (2010), Climate change effects on fishes and fisheries: towards a cause-and-effect understanding, *Journal of Fish Biology*, 77(8), 1745-1779, doi:10.1111/j.1095-8649.2010.02783.x.
- Przeslawski, R., S. Ahyong, M. Byrne, G. Wörheide, and P. Hutchings (2008), Beyond corals and fish: the effects of climate change on noncoral benthic invertebrates of tropical reefs, *Global Change Biology*, *9999*(9999), doi:10.1111/j.1365-2486.2008.01693.x.
- Rae, J. W. B., G. L. Foster, D. N. Schmidt, and T. Elliott (2011), Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system, *Earth Planet. Sci. Lett.*, *302*(3-4), 403-413, doi:10.1016/j.epsl.2010.12.034.
- Raven, J., K. Caldeira, H. Elderfield, O. Hoegh-Guldberg, P. S. Liss, U. Riebesell, J. Shepherd, C. Turley, and A. Watson (2005), Ocean acidification due to increasing atmospheric carbon dioxide, 68 pp, The Royal Society, London.
- Riddle, M. J., B. Tilbrook, I. Snape, K. Paterson, K. Berry, and D. B. Gore (2008), Deep, cold-water coral communities in Antarctica may be early indicators of the wider impacts of ocean acidification on coral-based ecosystems, in *Climate Change Monitoring Symposium*, edited, University of Sydney.
- Ridgwell, A., and D. N. Schmidt (2010), Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release, *Nature Geoscience*, *3*(3), 196-200, doi:10.1038/ngeo755.
- Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe, and F. M. M. Morel (2000), Reduced calcification of marine plankton in response to increased atmospheric CO₂, *Nature*, 407, 364-367, doi:10.1038/35030078.
- Riebesell, U. (2004), Effects of CO₂ enrichment on marine phytoplankton, *Journal of Oceanogaphy.*, *60*(4), 719-729, doi:10.1007/s10872-004-5764-z.
- Riebesell, U., and P. D. Tortell (2011), Effects of ocean acidification on pelagic organisms and ecosystems, in *Ocean Acidification*, edited by J.-P. Gattuso and L. Hanson, pp. 99-122, Oxford University Press, New York.
- Ries, J. B., A. L. Cohen, and D. C. McCorkle (2009), Marine calcifiers exhibit mixed responses to CO₂-induced ocean acidification, *Geology*, *37*(12), 1131-1134, doi:10.1130/g30210a.1.
- Roberts, D., W. R. Howard, A. D. Moy, J. L. Roberts, T. W. Trull, S. G. Bray, and R. R. Hopcroft (2011), Interannual pteropod variability in sediment traps deployed above and below the aragonite saturation horizon in the Sub-Antarctic Southern Ocean, *Polar Biology*, 34(11), 1739-1750, doi:10.1007/s00300-011-1024-z.
- Rodney, W. S., and K. T. Paynter (2006), Comparisons of macrofaunal assemblages on restored and non-restored oyster reefs in mesohaline regions of Chesapeake Bay

in Maryland, *Journal of Experimental Marine Biology and Ecology*, *335*(1), 39-51, doi:10.1016/j.jembe.2006.02.017.

- Rodolfo-Metalpa, R., S. Martin, C. Ferrier-Pagès, and J. P. Gattuso (2010), Response of the temperate coral *Cladocora caespitosa* to mid- and long-term exposure to pCO₂ and temperature levels projected for the year 2100 AD, *Biogeosciences*, 7(1), 289-300
- Roger, L.M., McKinnon, A.D., Knott, B., Matear, R., Scadding, C., Richardson, A.J. (2012) Comparison of shell structure of two tropical thecosomata (*Creseis acria* and *Diacavolinia longirostris*) from 1963-2009: potential implications of declining aragonite saturation state. *ICES Journal of Marine Science* 69: 465-474
- Roleda, M. Y., P. W. Boyd, and C. L. Hurd (2012), Before Ocean Acidification: Calcifier Chemistry Lessons, *Journal Of Phycology*, no-no, doi:10.1111/j.1529-8817.2012.01195.x.
- Russell, B. D., J.-A. I. Thompson, L. J. Falkenberg, and S. D. Connell (2009), Synergistic effects of climate change and local stressors: CO₂ and nutrient-driven change in subtidal rocky habitats, *Global Change Biology*, *15*(9), 2153-2162, doi:10.1111/j.1365-2486.2009.01886.x.
- Russell, B. D., C. D. G. Harley, T. Wernberg, N. Mieszkowska, S. Widdicombe, J. M. Hall-Spencer, and S. D. Connell (2011a), Predicting ecosystem shifts requires new approaches that integrate the effects of climate change across entire systems, *Biology Letters*, doi:10.1098/rsbl.2011.0779.
- Russell, B. D., C. A. Passarelli, and S. D. Connell (2011b), Forecasted CO₂ modifies the influence of light in shaping subtidal habitat, *Journal of Phycology*, *47*, 744-752, doi:10.1111/j.1529-8817.2011.01002.x.
- Sabine, C. L., R. A. Feely, N. Gruber, R. M. Key, K. Lee, J. L. Bullister, R. Wanninkhof, C. S. Wong, D. Wallace, B. Tilbrook, F. J. Millero, T. H. Peng, A. Kozyr, T. Ono, and A. F. Rios (2004), The oceanic sink for anthropogenic CO₂, *Science*, 305, 367-371, doi:10.1126/science.1097403.
- Sabine, C. L., and T. Tanhua (2010), Estimation of Anthropogenic CO₂ Inventories in the Ocean, *Annual Review of Marine Science*, 2(1), 175-198, doi:10.1146/annurev-marine-120308-080947.
- Santos, I. R., R. N. Glud, D. Maher, D. Erler, and B. D. Eyre (2011), Diel coral reef acidification driven by porewater advection in permeable carbonate sands, Heron Island, Great Barrier Reef, *Geophysical Ressearch Letters*, 38(3), L03604, doi:10.1029/2010gl046053.
- Sanyal, A., N. G. Hemming, G. N. Hanson, and W. S. Broecker (1995), Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera, *Nature*, *373*, 234-236
- Schiebel, R. (2002), Planktic foraminiferal sedimentation and the marine calcite budget, *Global Biogeochemical Cycles*, *16*(4), 1065, doi:10.1029/2001GB001459.
- Schlegel, P., J. N. Havenhand, M. R. Gillings, and J. E. Williamson (in press), Individual variability in reproductive success determines winners and losers under ocean acidification, *PLoS ONE*
- Schuiling, R., and P. Krijgsman (2006), Enhanced Weathering: An Effective and Cheap Tool to Sequester CO₂, *Climate Change*, *74*(1), 349-354, doi:10.1007/s10584-005-3485-y.
- Seidel, M. P., M. D. DeGrandpre, and A. G. Dickson (2008), A sensor for in situ indicator-based measurements of seawater pH, *Marine Chemistry*, 109(1-2), 18-28, doi:10.1016/j.marchem.2007.11.013.

Shaw, E. C., B. I. McNeil, and B. Tilbrook (2012), Impacts of ocean acidification in naturally variable coral reef flat ecosystems, *Journal of Geophysical Research*, *117*(C3), C03038, doi:10.1029/2011jc007655.

Sheppard Brennand, H., N. Soars, S. A. Dworjanyn, A. R. Davis, and M. Byrne (2010), Impact of Ocean Warming and Ocean Acidification on Larval Development and Calcification in the Sea Urchin <italic>Tripneustes gratilla</italic>, *PLoS ONE*, 5(6), e11372, doi:10.1371/journal.pone.0011372.

Shi, D., Y. Xu, B. M. Hopkinson, and F. M. M. Morel (2010), Effect of Ocean Acidification on Iron Availability to Marine Phytoplankton, *Science*, 327(5966), 676-679, doi:10.1126/science.1183517.

Silverman, J., B. Lazar, and J. Erez (2007), Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef, *Journal of Geophysical Research*, *112*, C05004, doi:10.1029/2006JC003770.

Silverman, J., B. Lazar, L. Cao, K. Caldeira, and J. Erez (2009), Coral reefs may start dissolving when atmospheric CO₂ doubles, *Geophysical Ressearch Letters*, *36*, L05606, doi:10.1029/2008GL036282.

- Simpson, S. D., P. L. Munday, M. L. Wittenrich, R. Manassa, D. L. Dixson, M. Gagliano, and H. Y. Yan (2011), Ocean acidification erodes crucial auditory behaviour in a marine fish, *Biology Letters*, 7(6), 917-920, doi:10.1098/rsbl.2011.0293.
- Singh, A. D., and S. M.-H. Conan (2008), Aragonite pteropod flux to the Somali Basin, NW Arabian Sea, *Deep Sea Res. Part I*, 55(5), 661-669, doi:10.1016/j.dsr.2008.02.008.
- Sinutok, S., R. Hill, M. A. Doblin, R. Wuhrer, and P. J. Ralph (2011), Warmer more acidic conditions cause decreased productivity and calcification in subtropical coral reef sediment-dwelling calcifiers, *Limnology & Oceanography*, 56(4), 1200-1212, doi:10.4319/lo.2011.56.4.1200.
- Smith, A. M., M. M. Key, and D. P. Gordon (2006), Skeletal mineralogy of bryozoans: Taxonomic and temporal patterns, *Earth-Science Reviews*, 78(3-4), 287-306, doi:10.1016/j.earscirev.2006.06.001.
- Smith, A. M. (2009), Bryozoans as southern sentinels of ocean acidification: a major role for a minor phylum, *Marine and Freshwater Research*, 60(5), 475-482, doi:10.1071/MF08321.
- Smith, A. M., and E. Girvan (2010), Understanding a bimineralic bryozoan: Skeletal structure and carbonate mineralogy of *Odontionella cyclops* (Foveolariidae: Cheilostomata: Bryozoa) in New Zealand, *Palaeogeography, Palaeoclimatology*, *Palaeoecology*, 289(1-4), 113-122, doi:10.1016/j.palaeo.2010.02.022.
- Smith, A. M., and E. I. Lawton (2010), Growing up in the temperate zone: Age, growth, calcification and carbonate mineralogy of *Melicerita chathamensis* (Bryozoa) in southern New Zealand, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 298(3-4), 271-277, doi:10.1016/j.palaeo.2010.09.033.
- Steinacher, M., F. Joos, T. L. Frölicher, G. K. Plattner, and S. C. Doney (2009), Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model, *Biogeosciences*, 6(4), 515-533
- Stumpp, M., J. Wren, F. Melzner, M. C. Thorndyke, and S. T. Dupont (2011), CO₂induced seawater acidification impacts sea urchin larval development I: Elevated metabolic rates decrease scope for growth and induce developmental delay, *Comparative Biochemistry and Physiology - Part A: Molecular & Integrative Physiology*, 160(3), 331-340, doi:10.1016/j.cbpa.2011.06.022.

- Sunday, J. M., R. N. Crim, C. D. G. Harley, and M. W. Hart (2011), Quantifying Rates of Evolutionary Adaptation in Response to Ocean Acidification, *PLoS ONE*, 6(8), e22881, doi:10.1371/journal.pone.0022881.
- Takeuchi, I. (1972), Food animals collected from the stomachs of three salmonoid fishes (Oncorhynchus) and their distribution in the natural environments in the northern North Pacific, *Bulletin of the Hokkaido Region Fisheries Research Laboratory*, *3*, 1-119
- Tans, P., and R. F. Keeling (2011), Trends in Atmospheric Carbon Dioxide, www.esrl.noaa.gov/gmd/ccgg/trends/.
- Tanzil, J. T. I., B. E. Brown, A. W. Tudhope, and R. P. Dunne (2009), Decline in skeletal growth of the coral *Porites lutea* from the Andaman Sea, South Thailand between 1984 and 2005, *Coral Reefs*, 28, 519-528, doi:10.1007/s00338-008-0457-5.
- Tortell, P. D., J. R. Reinfelder, and F. M. M. Morel (1997), Active uptake of bicarbonate by diatoms, *Nature*, *390*(6657), 243-244
- Tsurumi, M., D. L. Mackas, F. A. Whitney, C. DiBacco, M. D. Galbraith, and C. S. Wong (2005), Pteropods, eddies, carbon flux, and climate variability in the Alaska Gyre, *Deep Sea Research Part II*, 52(7-8), 1037-1053, doi:10.1016/j.dsr2.2005.02.005.
- Tunnicliffe, V., K. T. A. Davies, D. A. Butterfield, R. W. Embley, J. M. Rose, and W.
 W. Chadwick Jr (2009), Survival of mussels in extremely acidic waters on a submarine volcano, *Nature Geoscience*, 2(5), 344-348, doi:10.1038/ngeo500.
- Turley, C., M. Eby, A. J. Ridgwell, D. N. Schmidt, H. S. Findlay, C. Brownlee, U. Riebesell, V. J. Fabry, R. A. Feely, and J. P. Gattuso (2010), The societal challenge of ocean acidification, *Marine Pollution Bulletin*, 60(6), 787-792, doi:10.1016/j.marpolbul.2010.05.006.
- Uthicke, S., and K. Fabricius (2012), Productivity gains do not compensate for reduced calcification under near-future ocean acidification in the photosynthetic benthic foraminifera *Marginopora vertebralis*, *Global Change Biology*, doi:10.1111/j.1365-2486.2012.02715.x.
- Venn, A., E. Tambutté, M. Holcomb, D. Allemand, and S. Tambutté (2011), Live Tissue Imaging Shows Reef Corals Elevate pH under Their Calcifying Tissue Relative to Seawater, *PLoS ONE*, 6(5), e20013, doi:10.1371/journal.pone.0020013.
- Veron, J. E. N., O. Hoegh-Guldberg, T. M. Lenton, J. M. Lough, D. O. Obura, P. Pearce-Kelly, C. R. C. Sheppard, M. Spalding, M. G. Stafford-Smith, and A. D. Rogers (2009), The coral reef crisis: The critical importance of <350 ppm CO₂, *Marine Pollution Bulletin*, 58(10), 1428-1436, doi:10.1016/j.marpolbul.2009.09.009.
- Vichi, M., N. Pinardi, and S. Masina (2007), A generalized model of pelagic biogeochemistry for the global ocean ecosystem. Part I: Theory, *Journal of Marine Systems*, 64(1-4), 89-109, doi:10.1016/j.jmarsys.2006.03.006.
- Walther, K., K. Anger, and H. O. Pörtner (2010), Effects of ocean acidification and warming on the larval development of the spider crab *Hyas araneus* from different latitudes (54° vs. 79°N), *Marine Ecology Progress Series*, 417, 159-170, doi:10.3354/meps08807.
- Wei, G., M. T. McCulloch, G. Mortimer, W. Deng, and L. Xie (2009), Evidence for ocean acidification in the Great Barrier Reef of Australia, *Geochim. Cosmochim. Acta*, 73(8), 2332-2346, doi: 10.1016/j.gca.2009.02.009.
- Wernberg, T., B. D. Russell, P. J. Moore, S. D. Ling, D. A. Smale, A. Campbell, M. A. Coleman, P. D. Steinberg, G. A. Kendrick, and S. D. Connell (2011), Impacts of

climate change in a global hotspot for temperate marine biodiversity and ocean warming, *Journal of Experimental Marine Biology and Ecology*, 400(1-2), 7-16, doi:10.1016/j.jembe.2011.02.021.

Witt, V., C. Wild, K. R. N. Anthony, G. Diaz-Pulido, and S. Uthicke (2011), Effects of ocean acidification on microbial community composition of, and oxygen fluxes through, biofilms from the Great Barrier Reef, *Environmental Microbiology*, *13*(11), 2976-2989, doi:10.1111/j.1462-2920.2011.02571.x.

Wood, R. (1995), The changing biology of reef-building, Palaios, 10, 517-529

- Yu, J., H. Elderfield, and B. Hönisch (2007), B/Ca in planktonic foraminifera as a proxy for surface seawater pH, *Paleoceanography*, 22, PA2202, doi:10.1029/2006PA001347.
- Zachos, J. C., U. Rohl, S. A. Schellenberg, A. Sluijs, D. A. Hodell, D. C. Kelly, E. Thomas, M. Nicolo, I. Raffi, L. J. Lourens, H. McCarren, and D. Kroon (2005), Rapid Acidification of the Ocean During the Paleocene-Eocene Thermal Maximum, *Science*, *308*(5728), 1611-1615, doi:10.1126/science.1109004.