The UK Ocean Acidification Research Programme - Science Plan (2009-2014)

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1. Summary

In the last decade there has been growing scientific concern over changing ocean carbonate chemistry caused by ocean uptake of anthropogenic atmospheric carbon dioxide (CO_2) and how this will affect marine organisms, biodiversity, biogeochemistry, habitats and ecosystems. This knowledge has been exchanged with policy makers and stakeholders and there have been calls to reduce uncertainties in effects of and responses to future ocean acidification (Royal Society 2005; Turley *et al. 2006*; IPCC 2007). The *UK Ocean Acidification Research Programme* is a response to this need with £12M funding from NERC, the Department for Environment, Food and Rural Affairs (Defra) and the Department of Energy and Climate Change (DECC). This 5 year programme will address the policy and societal need for a greater understanding of the implications of ocean acidification and its risks to marine biogeochemistry and biodiversity and impact on the whole Earth System, through the delivery of seven *Science Deliverables.* Programme activities (excluding global scale modelling) will be focused on the North-East Atlantic (including European shelf and slope), Southern and Arctic Oceans. The programme will encourage strong collaboration, where appropriate, with other national and international programmes, primarily the newly funded German ocean acidification programme (BIOACID, Annex 1) and the EU Programmes (EPOCA and MEECE, Annex 2), to maximise the delivery of the programme's *Objectives*.

2. The Research Programme's Objectives

a. To reduce uncertainties in predictions of carbonate chemistry changes and their effects on marine biogeochemistry, ecosystems and other components of the Earth System.
b. To understand the responses to ocean acidification and other climate change related stressors by marine organisms, biodiversity and ecosystems and to improve understanding of their resistance or susceptibility to acidification.
c. To provide data and effective advice to policy makers and managers of marine bioresources on the possible size and timescale of risks to allow for development of appropriate mitigation and adaptation strategies.

3. Scientific Background

Over the last 200 years the oceans have absorbed about 25% of the CO_2 emitted into the atmosphere from human activities, effectively reducing CO_2 in the atmosphere and therefore buffering climate change (Sabine *et al.* 2004). This has resulted in the measurable alteration of surface ocean *p*H and the concentrations of CO_2, bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}), as well as the reduction of the saturation state and movement of the saturation horizons of calcium carbonate ($CaCO_3$) minerals towards the ocean surface (shoaling). This change in ocean carbonate chemistry is termed "Ocean Acidification" and is increasing in response to rising atmospheric CO_2. Since pre-industrial times ocean *p*H has decreased by a global average of 0.1 (equivalent to a 30% increase in acidity) (Caldeira and Wickett 2003) and unmitigated CO_2 emissions will cause ocean *p*H to decrease by as much as 0.40 in total by the year 2100 and 0.77 by 2300 (Caldeira and Wicket 2003). These will be the most rapid and greatest changes in ocean carbonate chemistry experienced by marine ecosystems for tens of millions of years (Caldeira and Wickett 2003). It will take tens of thousands of years for the changes in ocean chemistry to be buffered through neutralization by calcium carbonate sediments (Archer & Brovkin 2008, Ridgwell & Zeebe 2005) though the level at which ocean pCO_2 will eventually stabilize will be lower than it currently is (Archer & Brovkin 2008, Ridgwell & Zeebe 2005). Ocean acidification is a large-scale, long-term problem and with unmitigated CO_2 emissions is likely to result in widespread impacts on ocean biogeochemistry, biodiversity and the services that the oceans provide to the whole Earth System (Royal Society 2005, MCCIP 2009).

Already, shoaling of the aragonite saturation horizon (ASH) may be bringing increasingly corrosive waters to the productive, shallower shelf seas along the western coast of North America (Feely *et al.* 2008). Deep water forming in the North Atlantic is already reflecting the lowered *p*H conditions due to anthropogenic CO_2. Organisms which live in deep waters with aragonite skeletons, such as cold water corals abundant off the coast of Northern Europe, may be particularly vulnerable to shoaling of the ASH (Guinotte *et al*. 2006). Shelf sea models project similar rates and levels of acidification in European waters to those predicted for the global ocean (Blackford and Gilbert 2007), so ocean acidification may represent a substantial risk to commercially important fisheries and aquaculture. If we continue to emit CO_2 at the same rate, models project that parts of the Southern Ocean will be undersaturated in the important carbonate mineral aragonite (used by many organisms such as pteropods to make their shells) by the middle of this century with the whole of the Southern Ocean undersaturated by 2100 (Orr *et al.* 2005). In the Arctic Ocean aragonite undersaturation is projected to occur earlier (Steinacher *et al.* 2008) with 10% of its waters undersaturated in the next decade (Orr *et al.* 2008). By 2060 80% of Arctic waters are projected to be undersaturated in both aragonite and calcite (another key carbonate mineral used by organisms such as clams to make their shells). Calcifying organisms are likely to find calcification in these corrosive waters increasingly metabolically demanding and the consequences to food webs are of great concern. Measurable impacts may occur earlier than this due to a lowering of the carbonate ion concentration impacting calcification and other processes, but our knowledge of these is currently too sparse to make predictions.

Laboratory experiments, field observations of natural CO_2 rich seawater and studies of previous ocean acidification events in Earth's history indicate that these changes are a threat to the survival of organisms that use $CaCO_3$ to produce shells, tests and skeletons (see references in Kleypas *et al.* 2006, Fabry *et al.* 2008: Doney *et al.* 2009). However, not all studies have shown this (e.g., Iglesias-Rodriguez *et al*. 2008) therefore, this is a controversial area (Riebesell *et al.* 2008) needing resolution especially as data is required by Earth System Models to predict pelagic calcification and its consequences (Ridgwell *et al.* 2009). Other experiments reveal that other biological processes are also vulnerable to predicted future changes to ocean chemistry. Changes to ocean biogeochemistry may have a direct feedback to the Earth system and to climate through carbon and nutrient cycles and air-sea gas exchange (Feely *et al.* 2009, Turley *et al.* 2009).

Given specific CO_2 emission scenarios, predictions of future ocean carbonate chemistry are relatively certain at the global scale. Nonetheless, recent observations of inter-annual and long-term variation in ocean CO_2 uptake suggest that future regional ocean acidification and ocean carbonate chemistry are less well understood. A major challenge is assessing the risk of ocean acidification on marine food webs, ecosystems and ocean biogeochemistry because of their complexity. Another challenge is reducing uncertainty in the sensitivity of key biogeochemical cycles. An understanding of previous ocean acidification events in Earth's history will provide useful insights into extinctions or adaptation strategies.

A concerted, multi-disciplinary effort, in collaboration with other nations, will improve our understanding and increase certainty in predictions of impacts and risks of ocean acidification.

The impact of ocean acidification on biogeochemistry and biodiversity and subsequent feedbacks on climate will depend on the rate and magnitude of changes in ocean chemistry, so it is important for the programme to consider different scenarios (section 5, *Implementation Plan*) of future CO_2 emissions to give useful projections and advice to policy makers. In particular, experimental work will consider the effects of acidification at different atmospheric CO_2 concentrations (section 5, Implementation Plan) and modelling will consider different CO_2 emission scenarios (both mitigated and unmitigated). Ocean acidification is the partner to climate change, so identification of the effects of multiple stressors, e.g. increased temperature as well as acidification, and their combined impacts and feedbacks on ocean biogeochemistry, biodiversity, and climate is essential.

4. Strategic Context

The UK has played a major role in bringing the potentially serious consequences of ocean acidification to the attention of national and international stakeholders. The Royal Society (2005) in its Report on ocean acidification called for a rapid investment by stakeholders, equivalent to that of climate change and called on climate change policy makers to consider ocean acidification in their CO_2 emission reduction targets. The IPCC (2007) 4^{th} Assessment Report on Climate Change also states, for the first time, that increasing anthropogenic CO_2 will result in increased acidity of the world's oceans. Since then the Scientific Advisory Board for the German Government for Climate change (WGBU) reported on the significance of ocean acidification and paved the way for the funding of the German programme "**Bio**logical Impacts of Ocean **Acid**ification" (BIOACID, Annex 1). The European Union in its 7^{th} Framework Programme recognised the importance of ocean acidification and issued a call for proposals resulting in the funding of the "**E**uropean **P**roject on **Oc**ean **A**cidification" (EPOCA, Annex 2) and "**M**arine **E**cosystem **E**volution in a **C**hanging **E**nvironment" (MEECE, Annex 2). Other programmes addressing the topic are emerging, e.g. USA Senate Bills on ocean acidification, which will increase this investment. IGBP, UNESCO and SCOR recognised the importance of ocean acidification and supported the series of symposia *"Oceans in a High CO_2 World"*, the second of which, held in Monaco in October 2008, resulted in *"The Monaco Declaration"* (http://ioc3.unesco.org/oanet/HighCO2World.html). This called on climate change negotiators to take ocean acidification into account. Ocean acidification is a powerful additional argument for united global societal action in future climate change negotiations and an important driver for a change in UK and global energy policy.

The *UK Ocean Acidification Research Programme* will increase the understanding and awareness of the risk of ocean acidification to the marine ecosystem and therefore significantly contribute at this strategic level. The programme will address the need for scientific evidence for UK and international policy makers, for future assessments by IPCC and the UNFCCC, and input to Biodiversity Action Plans, the 'Marine & Coastal Access Bill' and The European Marine Strategy Framework Directive (MSFD).

5. NERC, Defra and DECC priorities and context

This Research Programme directly relates to delivery of the NERC Strategy (in particular Earth System Science and Biodiversity Science Themes) and the UK Government's Strategic Objectives with respect to adapting to, and mitigating climate change and ensuring a healthy, resilient, productive and diverse natural environment. It is anticipated that it will also make a significant contribution to Objective B of the *Living With Environmental Change* programme (http://www.lwec.org.uk/). In addition, the programme will take advantage of international collaboration opportunities, primarily with BIOACID and other appropriate European projects such as EPOCA and MEECE.

6. The Research Programme Science Deliverables

Programme *Objectives a and b* will be achieved through the seven *Science Deliverables* and *Objective c* will be achieved through the knowledge exchange (KE) activities (section 11, *Implementation Plan*). Activities (with the exception of global scale modelling) will be focused on regions where the UK has strong scientific and strategic interest and where logistics of access are relatively straightforward and cost effective, e.g. the Northeast Atlantic (including European shelf and slope), Southern and Arctic Oceans. A series of cruises using NERC's research ships is anticipated, as well as the use of ships of opportunity (section 7, *Implementation Plan*).

The seven *Science Deliverables* from the *UK Ocean Acidification Research Programme* are:

1: Improved estimates of ocean CO_2 uptake and associated acidification.
2: Improved understanding of the impact of ocean acidification on surface ocean biology, community structure, biogeochemistry and on feedbacks to the climate.
3: Identification and improved understanding of the potential impacts and implications of ocean acidification on key benthic ecosystems, communities, habitats, species and life cycles.
4: Improved understanding of the potential population, community and ecosystem impacts for all life stages for commercially important species and their capacity to resist and adapt.
5: Provision of evidence from the palaeo record of past changes in ocean acidity and resultant changes in marine species' composition and Earth System function.
6: Improved understanding of the cumulative/synergistic effects of ocean acidification and other global change pressures on ecosystems, biogeochemical cycles and feedbacks on climate through modelling activities.
7: A service for carbonate chemistry measurements.

The *Science Deliverables* are detailed below and will be implemented as specified in the *Implementation Plan.* The *Implementation Plan* also provides further details on standards and guidelines for CO_2 experiments in ocean acidification studies, data management requirements and science collaborations.

Science Deliverable 1: Improved estimates of ocean CO_2 uptake and associated acidification.

Aim 1.1 To quantify the rate of progression of ocean acidification in the North-East Atlantic (including European shelf and slope), Southern and Arctic Oceans, including identification of when/where $CaCO_3$ undersaturation will occur first.

Aim 1.2 To quantify spatial and/or seasonal variability of carbonate system parameters in these areas.

Aim 1.3 To improve quantification of the rate of oceanic CO_2 uptake in these areas.

It is essential to understand progressive changes in ocean acidification and ocean CO_2 uptake, the factors that control them, and how these processes may change in the future. High latitude oceans are particularly sensitive to ocean acidification (Bellerby *et al.* 2005, *Orr et al.* 2005).

Southern Ocean (Orr *et al.* 2005) and Arctic (Orr *et al.* 2008) surface waters are likely to become undersaturated with respect to aragonite in the first half of this century. Cold water corals in the North-East Atlantic (Guinotte et al. 2006) and the Nordic Seas (Bellerby, personal communication) are at risk of aragonite undersaturation, with Arctic surface waters becoming undersaturated over the next few decades (Orr *et al.* 2008), Steinacher *et al.* 2008). Localised aragonite undersaturation already occurs in upwelled shelf waters (Feely *et al.* 2008) and the low salinity Baltic Sea (Tyrrell *et al.* 2008). The important North Atlantic CO_2 sink varies over time (Schuster & Watson 2007), while the efficiency of the Southern Ocean CO_2 sink has decreased (Le Quéré *et al.* 2007, McNeil & Matear 2008). Additionally, seasonal variation of pCO_2 and pH in the oceans and shelf seas will increase as oceanic CO_2 uptake and associated ocean acidification continue (after Delille *et al.* 2005).

The *UK Ocean Acidification Research Programme* will improve the quantification of the marine carbonate system and oceanic CO_2 uptake in specific locations and on seasonal, interannual and longer time scales. Surface ocean and atmosphere carbon observing systems have proven well suited to constraining the ocean CO_2 sink on seasonal to decadal timescales (IOCCP, 2007). To determine fully the marine carbonate system this deliverable will accurately analyse at least two carbonate parameters out of the four (see section 5, *Implementation Plan* for further details).

Science Deliverable 2: Improved understanding of the impact of ocean acidification on surface ocean biology, community structure, biogeochemistry and on feedbacks to the climate.

Aim 2.1 To ascertain the impact of ocean acidification on planktonic organisms, both in terms of physiological impacts and also population abundances and community composition.

Aim 2.2 To quantify the impacts of ocean acidification on biogeochemical processes affecting the ocean carbon cycle, including via availability of bio-limiting nutrients.

Aim 2.3 To determine impacts of ocean acidification on the air-sea flux of climate active gases and on the composition of organics in the microlayer.

The role of this deliverable is to reduce uncertainty about how ocean acidification will impact on biogeochemical and climate relevant processes. Impacts may occur both directly through changes to physiological rates per organism, and also through altered abundances of process relevant organisms and induced changes to community composition. To achieve this deliverable, the study of biogeochemical and climate impacts will therefore be closely integrated with study of plankton diversity and population abundances. This deliverable will focus on those biogeochemical processes vulnerable to ocean acidification.

Calcification is an important biogeochemical process carried out by microscopic planktonic organisms and is still poorly understood. For instance, a large number of studies have found reduced calcification and increased incidence of shell malformations in microscopic plants, called coccolithophores, grown at high CO_2 (Riebesell *et al.* 2000; Zondervan *et al.* 2002; Delille *et al.* 2005; Engel *et al.* 2005; Sciandra *et al.* 2003; Langer *et al.* 2006; Feng *et al.* 2008). However, a smaller number of experiments have not found this (Langer *et al.* 2006, Iglesias-Rodriguez *et al.* 2008) with these results contested by Riebesell *et al.* (2008). Since Earth System Models require data from such experimentation to predict pelagic calcification and its consequences it is important for this programme to understand and better parameterise this process (Ridgwell *et al.* 2009).

Energy expended on growth and respiration are key to the relative success of different groups of planktonic organisms. Contrasting results have been obtained in terms of carbon uptake, growth rates and nutrient uptake ratios (carbon:nitrogen and carbon:phosphorus) by different groups of phytoplankton under high CO_2 conditions (Riebesell *et al.* 1993, Rost & Riebesell 2004, Leonardos & Geider 2005, Riebesell *et al.* 2007, Rost *et al.* 2008, Tortell *et al.* 2008). This programme will clarify these results and explore their significance on population abundance and community composition. There is a lack of published evidence on effects of ocean acidification on respiration which will also be addressed.

Zooplankton are an important link in the food web and so their vulnerability to ocean acidification is important to assess. However, there are relatively few laboratory studies on zooplankton, although studies undertaken show some groups, e.g. foraminifera and pteropods, to be sensitive (Orr *et al.* 2005, Kleypas *et al.* 2006, Moy *et al.* 2009). For instance chemical corrosion of new shell growth has been observed in pteropods exposed to high CO_2 conditions (Orr *et al.* 2005). In contrast, another study detected effects on copepod hatching success only under conditions more extreme than those predicted for the future (Mayor *et al.* 2007) so on the whole they appear relatively tolerant (Kurihara & Ishimatsu 2008) of lower *p*H. Larvae of some species, such as echinoderm larvae which spend only part of their life cycle in the water column, may be particularly sensitive (Dupont *et al.* 2008). This programme will look at the relative sensitivity of key zooplankton species and subsequent impact on community composition.

Ocean acidification might also affect key biogeochemical processes that drive the ocean carbon and nutrient cycles. For instance, the means of long-term sequestration of carbon into the deep ocean via the biological carbon pump could be vulnerable and will be investigated in this programme. This could be via direct impact on plankton composition or indirectly through effects on nutrient supply. Studies have found large increases in photosynthesis, N_2 fixation and even growth rates in the important nitrogen fixer *Trichodesmium* with increasing CO_2 (Barcelos e Ramos *et al.* 2007; Hutchins *et al.* 2007; Levitan *et al.* 2007), which could have significant impacts on nutrient availability. It has been argued (de Baar 2008) that the effects on trace metal and macro-nutrient inorganic chemical speciation via lowered *p*H will not be significant in open ocean waters, except for the NH_3/NH_4^+ couple, suggesting that air-sea fluxes of ammonia may alter due to both direct and indirect ocean acidification effects. Ocean acidification induced alleviation of iron limitation in High Nitrogen Low Chlorophyll (HNLC) waters (~30% of the global ocean) seems unlikely, unless changes in organic complexation are induced (de Baar 2008). This deliverable will investigate the effect of ocean acidification on nutrient supply and help inform *Deliverable 6.*

The oceans and shelf seas act as a source and/or sink of gases other than CO_2 that are known to be important in atmospheric chemistry via their roles in radiative transfer, e.g. nitrous oxide (N_2O), tropospheric oxidation capacity, e.g. oxygenated volatile organic compounds (OVOCs) and volatile iodine compounds (VICs) and the ozone chemistry of the stratosphere, e.g. methyl bromide. Further, the oceans are believed to act as major sources of cloud condensation nuclei via the supply of organics from the sea surface and dimethyl sulphide (DMS) from marine phytoplankton. Several studies have shown that concentrations of DMS, and its precursor DMSP, can be significantly reduced under high pCO_2 conditions (Avgoustidi 2006, Hopkins *et al.* 2009) but not always (Vogt *et al.* 2008). A mesocosm experiment has also shown that net production of VICs in seawater can be significantly reduced at high pCO_2 (Hopkins *et al.* 2009). Little work has been reported on other climate relevant gases. However, preliminary work suggests that the ratio of nitrification to denitrification is sensitive to ocean acidification (Rees *et al.* 2009) indicating that the production of N_2O in seawater may well be altered, as this gas is an intermediate species in both pathways. It is clearly important that this programme helps resolve the impact of ocean acidification on nitrification/denitrification and climate reactive gases.

Additionally, there is some evidence from mesocosm experiments that the formation of transparent exopolymer particles increases under high pCO_2 conditions (Riebesell *et al.* 2007). An increase in, or even change in the composition of, organic compounds in the sea surface microlayer could impact not only on air-sea gas transfer rates, but also on the formation of organic aerosol, and is an area worthy of further investigation in this deliverable.

Science Deliverable 3: Identification and improved understanding of the potential impacts and implications of ocean acidification on key benthic ecosystems, communities, habitats, species and life cycles.

Aim 3.1 To determine the effect of ocean acidification on the performance, life history and population dynamics of individual benthic species, with preference given to those species likely to influence overall benthic ecosystem function.

Aim 3.2 To quantify the impacts of ocean acidification on biogeochemical cycling of key nutrients within sediments and their exchange with the seawater column.

Aim 3.3 To determine the effects of ocean acidification on the overall function of key benthic habitats.

The response of assemblages or ecosystems to environmental change or stressors depends on the response of the individuals that make up system (Fabry *et al.* 2008; Widdicombe & Spicer 2008). Recent developments in benthic and pelagic mesocosm technology have helped to close the gap between small scale laboratory experiments and field observations (Widdicombe *et al.* 2009, Riebesell *et al.* 2008). Powerful insights may also be gained from studies of areas with natural CO_2 enrichment (Hall-Spencer *et al.* 2008).

In this programme species will be selected, where the physiological challenges posed by acidification can best be resolved, or where organisms have a strong influence on ecosystem function. A critical aspect here will be the integration of traditional physiology and ecology with the rapidly developing field of functional genomics (Hofmann *et al.* 2008). The impacts of ocean acidification are likely to differ between those species with a significant carbonate skeleton (calcifiers) and those without, whilst within calcifiers there will also likely be differences between those producing skeletons of aragonite and those utilising calcite. This programme therefore attaches importance to coverage of a broad phylogenetic spectrum, so as to avoid the problem of conclusions being biased by concentration on a few model groups (particularly if those selected for study are particularly susceptible to acidification). Where model organisms are chosen, consideration should be given to those which have been, or soon will be, genetically sequenced. The long generation time of many marine organisms makes the study of adaptation potential across generations difficult. It will be important therefore to direct some attention toward those organisms with more rapid reproductive turnover, e.g. microbial, meiofaunal and smaller macrofaunal organisms. In selecting target organisms, priority will be given to work on organisms that complement work planned within the BIOACID and EPOCA programmes.

Critical aspects for this deliverable will be to resolve the effect of ocean acidification on the calcification process itself (Orr *et al.* 2005), and also the energetic cost of acclimation or adaptation either through direct measures such as metabolism or through indirect effects on energetics (Findlay *et al.* 2009). The latter could be important, since changes in energy budget have the potential to affect key aspects of population dynamics such as growth, reproductive output and performance (Wood *et al.* 2008). Since both ocean acidification itself, and its metabolic impacts will be affected synergistically by temperature (Pörtner 2008, Pörtner *et al.* 2009) it will be important to undertake studies in a variety of environments and this programme has identified the polar regions as particularly important in this regard as this may be where changes in seawater carbonate chemistry are likely to occur first (Gangsto *et al.* 2008).

Although many organisms do not produce a skeleton with significant carbonate content, all marine organisms maintain an internal milieu that depends on exchange of ions with the environment. Elevated levels of CO_2 have the potential to affect these exchange processes, and thereby the cost of maintaining internal acid-base balance (Pörtner 2008). It is therefore important for this programme to investigate the synergistic impact of ocean warming and acidification on the costs of homeostasis in both calcifiers and non-calcifiers. In many marine organisms, sensitivity to environmental perturbation can vary with life-stage, with the early stages such as eggs or embryos more sensitive than the adult stages (Dupont & Thorndyke 2009). This programme therefore attaches importance to studies that cover the full life-cycle.

This programme will increase our understanding of the impact of ocean acidification on benthic biogeochemistry (*cf Science Deliverable 2*). There is preliminary evidence to suggest that ocean acidification will affect the cycling of nutrients within the sediment by changing the structure and function of microbial communities and thereby altering the coupling between nitrification and denitrification (Widdicombe & Needham 2007). These changes could also significantly affect benthic alkalinity generation (Thomas *et al.* 2008); an important source of alkalinity in coastal and shelf sediments. In addition, changes in the performance and distribution of key benthic organisms, in particular bioturbating species and the microphytobenthos, could have considerable implications for nutrient cycling within sediments and the supply of these nutrients to pelagic ecosystems in support of primary productivity (Wood *et al.* 2009).

Effects at the level of assemblages or ecosystems are clearly important for this programme to investigate, but far more difficult to determine. Species whose skeletons form the substrata for other organisms (ecosystem engineers) have the capacity to exert far-reaching effects and, as many of these are easy to sample and work with, would form an ideal experimental system. Examples of suitable systems include cold water coral (*Lophelia*) reefs, maerl beds, marine macroalgae and seagrass. Coastal and shelf (including shelf break) systems are important areas for study, because they are easy to access, but also because they are vulnerable and likely to exhibit early indications of impacts (Blackford *et al.* 2008). For the most complete picture, it will be necessary to examine both muddy and hard benthic ecosystems. To determine ecosystem scale effects such as trophic cascades or secondary effects within the food web, modelling approaches will be important, and emphasis will be placed on work that interacts with existing theoretical approaches to ecosystem structure and function.

Science Deliverable 4: Improved understanding of the potential population, community and ecosystem impacts for all life stages for commercially important species and their capacity to resist and adapt.

Aim 4.1 To examine the physiological and behavioural responses of commercial fish and shellfish to ocean acidification and their capacity to resist and adapt.

Aim 4.2 To 'scale up' from laboratory studies to population and stock level responses to ocean acidification including an analysis of possible socio-economic consequences. *Aim 4.3* To examine how changes in planktonic and benthic food-webs, as a result of ocean acidification, impact upon the production and yields of commercial fish and shellfish stocks. *Aim 4.4* To investigate the possible socioeconomic consequences relating to ocean acidification at an ecosystem level.

In the UK, shellfisheries now contribute more to the national economy than fisheries targeting fin-fish such as cod or herring (£271 million in 2007, versus £264 million). The most valuable shellfish species are those targeting *Nephrops* (scampi), scallops, crabs and lobsters, many of which may be severely impacted by ocean acidification in the future. Comparatively little research, including socio-economic studies, has been undertaken regarding the implications of ocean acidification on commercial fin-fish and shellfish (Fabry *et al.* 2008, Turley *et al.* 2009), both of which are of direct interest for human food provision. Potential impacts could be direct at the organism and population level or indirect through impacts to food webs.

There are indications, from laboratory experiments, that ocean acidification could have a direct negative economic impact on cultured mussels with observations of a dramatic reduction in shell formation (by 30 %) by adult mussels at *p*H levels that are likely to be reached this century (Gazeau *et al.* 2007). However, the response for adult oysters was significantly different with apparent tolerance even at very high levels of pCO_2. It is therefore important to study species specific differences in response and their capacity to resist and/or adapt. Additionally, early life stages can be more sensitive to environmental stressors, including ocean acidification (Dupont *et al.* 2008), so it is important to consider all aspects of an organism's life cycle when assessing population and stock level response to ocean acidification. Experiments have shown that many adult fishes are able to buffer against changes in pCO_2 and adapt relatively quickly (Larsen *et al* 1997; Pörtner *et al.* 1998) and may be less vulnerable than some benthic invertebrates. However, the physiology, metabolism, reproductive biology, behavioural patterns, cognitive abilities, feeding rates, prey selection and larval development of some fish may be significantly impaired and this would have serious consequences for long-term population survival and fisheries yields (Pörtner *et al.* 2004; Ishimatsu *et al.* 2004). Many commercially important fin-fish species rely heavily on benthic invertebrate species, e.g. bivalves, crabs and echinoderms, as a major food source and are therefore also likely to be indirectly impacted by ocean acidification. Additionally, as most fish larvae feed selectively on copepods and other planktonic invertebrates, year-class strength in many fin-fish species is highly dependent on the planktonic food sources available during this early life stage. In years where insufficient food is available, starvation mortality can be considerable and hence populations are impacted long into the future.

This deliverable will require a mixture of laboratory controlled investigations on adults and early life stages and their food sources as well as applying existing modelling frameworks (single species, multispecies, food webs, ecosystem) adapted to incorporate the outputs from the laboratory work. This will enable 'up-scaling' in order to assess the risk of ocean acidification impact upon the production and yields of commercial fish and shellfish in relation to other sources of mortality, including exploitation by fisheries, temperature effects or natural predators. *Science Deliverable 4* will involve a preliminary analysis of the possible socio-economic consequences of ocean acidification, including the valuation of ecosystem 'goods and services' and how these might be affected.

Science Deliverable 5: Provision of evidence from the palaeo record of past changes in ocean acidity and resultant changes in marine species' composition and Earth System function.

Aim 5.1 To determine whether historical changes in carbonate ion concentration and *p*H since industrialisation have already had discernible impacts on the calcification of marine organisms.

Aim 5.2 To ascertain the maximum rate and amplitude of ocean acidification to which species and ecosystems can adapt and the threshold of acidification that would lead to enhanced evolutionary turnover and extinction of species.

*Aim 5.*3 To assess suitability of museum collections for palaeo study of ocean acidification.

Modern ecosystems do not live in "pristine" non-acidified environments. Ocean acidification has already started to affect the ocean (Caldeira and Wicket, 2003; Orr *et al.*, 2005), and hence the ecological baseline for pre-industrial calcification is missing. The very recent geological record and historical collections will be used by this deliverable to answer the question of whether ocean acidification has already started to affect modern ecosystems and the species within them. These archives encompass plankton net, sediment trap or Continuous Plankton Recorder samples covering pelagic specimens over the last 30 years (e.g. Beaugrand *et al.* 2002, Zaric *et al.* 2005). These records can be augmented with high sedimentation rate cores and historical collections from expeditions such as the *Challenger* (1872 – 1876) and the *Discovery* (1901 – 1904). While these records will be very informative on the initial impacts of ocean acidification, they do not allow the potential for adaptation to be addressed, since this is a process taking hundreds to thousands of generations. The large time involved also makes it impractical to test the adaptation potential of different organisms in laboratory experiments, especially for long-lived, i.e. longer than a day or two, organisms. An early assessment of suitable museum collections for palaeo ocean acidification study will facilitate this.

Earth history records gradual but substantial long-term changes in global environmental change (Royer *et al.* 2004). The rate of change gave marine organisms thousands to millions of years to adapt and evolve in response to global environmental change, including changes in CO_2 and associated carbonate ions in the ocean. For example, glacial interglacial CO_2 changes of ~100 ppm, the same increase as in the last 100 years, occurred over several thousands of years, exposing species to a gradual change of CO_2 in the atmosphere (e.g. Siegenthaler *et al.* 2005) and hence saturation state change in the ocean. Studies of periods of relative stasis are likely to be less relevant if carbonate chemistry changes are not of comparable rate, direction and magnitude to those predicted for the next century (Panchuk *et al.* 2008, Ridgwell 2007, Zeebe and Zachos 2007). Rate as well as magnitude challenges the organisms' and ecosystems' ability to adapt to environmental changes (Buckling *et al.* 2003).

The geological record has preserved a series of abrupt ocean acidification events of different amplitude (Zachos *et al. 2001 &* 2004), such as the Palaeocene-Eocene hyperthermals. These abrupt events will therefore be a focus of this deliverable. These time intervals provide key information regarding the response of marine calcifiers to the warming and acidification (Sluijs *et al.* 2007, Thomas 2007) – migration of warm water taxa towards higher latitudes and increased evolutionary turnover in both calcareous phytoplankton (Gibbs *et al.* 2006) and zooplankton (Kelly *et al*. 1998). However, our ability to link the biotic changes in these events to ocean acidification, and hence help predict future ecosystem shifts and changes, is limited by the lack of precise, time-resolved *p*H and carbonate ion records for these events.

Thus the relationships between rates of chemical change and adaptation potential are not yet based on sound environmental data but on a series of model results. A series of possible carbonate ion proxies have been calibrated for recent ocean history, e.g. Zn/Ca (Marchitto *et al.* 2000), B/Ca (Yu & Elderfield 2007, Yu *et al.* 2007), size normalised weight (Barker & Elderfield 2002) and can provide important information to this deliverable about the precise nature of the environmental pressure on marine biota during times of rapid carbonate system change.

This programme will link studies of modern and fossil organisms which will strongly increase the interpretability of the palaeo record, and will alsoprovide important information on ecosystem and earth system scale effects. The characterisation of physiological differences between species unaffected by these perturbations, such as some coccolithophore species or agglutinated benthic foraminifers, versus groups which have undergone major evolutionary turnover will allow the identification of major vulnerabilities in the future.

Science Deliverable 6: Improved understanding of the cumulative/synergistic effects of ocean acidification and other global change pressures on ecosystems, biogeochemical cycles and feedbacks on climate through modelling activities.

Aim 6.1 To improve understanding of the combined impacts of ocean acidification and other global change pressures on ecosystems, biogeochemical cycles and feedbacks on climate at the global scale.

Aim 6.2 To improve understanding of the combined impacts of ocean acidification and other global change pressures on regional ecosystems and biogeochemical cycles.

Changes brought about by ocean uptake of anthropogenic CO_2 will impact on ecosystems and biogeochemical and climate relevant processes in various ways. For example, experimental evidence suggests that there will be significant organism and ecosystem responses to ocean acidification via processes such as planktonic calcification, carbon and nutrient assimilation and cycling and primary production. Acidification has also been shown to affect the early life stages of both benthic and pelagic higher trophic organisms. A consequence of this may be changes to ecosystem composition, size structure and succession, potentially resulting in changes to ecological structure, energy flow and biogeochemical pathways. Simultaneously, natural and anthropogenically induced climate change will lead to other changes in the Earth System, e.g. temperature, surface water stratification, nutrient distribution, the extension of oxygen minimum zones and turbidity of the surface waters, all of which are also likely to affect marine ecosystems, biogeochemical cycles and climate relevant processes. Direct anthropogenic drivers such as fishing, eutrophication and pollution are also likely to impact marine ecosystem structure and function. It is essential to assess the significance of ocean acidification on both the regional and global scale in the context of these other drivers.

Using coupled physical-ecosystem models for oceans and regions, which take account of physical transport, chemical and biological processes, the *UK Ocean Acidification Research Programme* will consider the combined effects of ocean acidification and other global change pressures on marine ecosystems, biogeochemical cycles and climate feedbacks and make assessments of possible future ecosystems. Building on existing regional and global modelling capabilities, the modelling approaches can be used to project changes in ocean pH, temperature, stratification and oxygen distribution under different greenhouse gas emission scenarios, which will in turn be used to assess the potential combined impacts of these changes on marine ecosystems, biogeochemistry and climate feedbacks. This will shed light on the potential magnitude and timescale of risks associated with future CO_2 emissions (including possible ‘tipping points’).

Experimental results are essential for parameterising both global and regional models' ecosystem responses, and it is therefore essential that work for this output is fully informed by experimental work in this field, including that undertaken for the other *Science Deliverables*. At the same time, the modelling results from this *Science Deliverable* can be used to inform experimental boundaries in the other *Science Deliverables*. Evaluating the indirect impacts of ocean acidification on atmospheric chemistry and climate system will require the use of results from a combination of laboratory experiments, mesocosm and field experiments as described in *Science Deliverable 2* and modelling in order to extrapolate results over wider spatial and temporal scales, to assess the impacts of multiple drivers and to develop an integrative and predictive capability of the impact of feedbacks from the ocean on atmospheric chemistry and climate.

Science Deliverable 7: A service for carbonate chemistry measurements
Aim 7.1 To provide high quality carbonate chemistry measurements across the programme.

The ability to study ocean acidification hinges on high quality measurements of carbonate chemistry, both for experimental studies and for observational work. Currently the UK does not have the capability to support the scale of analytical requirements for carbonate chemistry within the *UK Ocean Acidification Research Programme* so an investment to develop capacity is required.

Four parameters of the carbonate system can be measured DIC, alkalinity, pCO_2 and pH). Only pCO_2 and pH can be measured autonomously at present. The carbonate system has two degrees of freedom and therefore the whole carbonate system (including the saturation state of seawater with respect to calcite and aragonite) can be calculated from any two measurements, but not from only one. Different pairs of parameters give a different accuracy for the remaining carbonate parameters (Millero, 1995, Zeebe & Wolf-Gladrow 2001), with the DIC and alkalinity pair most often used. pH is difficult to measure to sufficient accuracy at present, for ocean acidification purposes (Millero 1995, Dickson *et al.* 2007). Use of cheap, 'off-the-shelf' pH sensors is strongly discouraged for most ocean acidification-related purposes, because high quality results are unlikely to be obtained (Orr *et al.* 2009). As pCO_2 and pH strongly co-vary they are not the ideal pair to measure for calculation of the carbonate system (Millero 1995, Orr *et al.* 2009).

Unfortunately DIC and alkalinity measurements are difficult and expensive to make to the required accuracy and precision, requiring for instance training of specialist staff and new equipment costing >£50k. These requirements make it impractical for many UK institutions to carry out their own DIC and alkalinity analyses. However, sample storage without compromising the chemistry is possible (Dickson et al. 2007) which means that a central service providing high-quality measurements of DIC and alkalinity through this deliverable will help ensure the quality of ocean acidification work in the UK, and make high quality ocean acidification work feasible for all institutions. Such a service will also provide benchmark standard measurements for comparative purposes, for institutions starting to develop their own capability.

7. Deliverables and Mechanisms

The *Science Deliverables* will provide greater understanding of the future impacts and implications of ocean acidification on the key aspects of marine biodiversity and biogeochemistry in *Objectives a* and *b* and provide policy related science to help decision makers (*Objective c*). To provide these deliverables and achieve the programme objectives there will be one open call for proposals for specific research projects to address the aims detailed for each of the *Science Deliverables*. A diverse range of activities from research ship based experiments and observations and monitoring on commercial ships, through mesocosm studies, to laboratory work and modelling can be undertaken. In addition, there will be a call for tender for key services and roles to support the programme (see *Implementation Plan*).

8. International Collaboration

By developing the *UK Ocean Acidification Research Programme* in collaboration with international partners the programme will achieve more than it would do alone. For example, this programme will have a far more ambitious experimental, fieldwork and modelling components. For this reason collaboration, where appropriate, is strongly encouraged with other national (German programme, BIOACID) and European projects (EPOCA and MEECE); see Annex 1 and 2 for details of these programmes and details of the contact scientists. This *Science Plan* has been developed to complement the BIOACID programme and to a lesser extent the EPOCA and MEECE projects. Collaboration will take the form of exchange visits to work together on laboratory and mesocosm experiments and on research cruises as well as student costs for the period of exchange. Joint annual meetings, shared workshops, a Reference User Group of key stakeholders and an intercalibration exercise for carbonate chemistry measurements have been agreed between the *UK Ocean Acidification Programme*, BIOACID and EPOCA (see *Implementation Plan*).

9. National Collaboration to Deliver Policy Relevant Science

This new five-year Research Programme is jointly funded by NERC, Defra and DECC. Collaborations between different UK science communities (HEIs, NERC Centres and UK Government Departments' marine laboratories) and disciplines are also encouraged to build a community of researchers and increase capacity. While ocean acidification is not the principal focus of any UK Research Programme, there is some ongoing research activity within UK Research Centres, for example BAS, NOCS, PML and SAMS, and universities, funded both by NERC and from other sources. Collaboration within this programme and with these other UK activities will be facilitated by the Science Co-ordinator as part of the programme activities (see *Implementation Plan*).

10. Capacity Development

The Research Programme aims to build a multidisciplinary community of scientists using observational, experimental and modelling techniques to investigate and assess the threats of current and future ocean acidification to ocean biogeochemistry, biodiversity and the whole Earth system including feedback to climate. Collaborations between different UK marine and Earth science communities (HEIs, NERC Centres and UK Government Departments' marine laboratories) will build a multidisciplinary community of researchers and increase capacity in ocean acidification research. There is a clear scientific benefit in bringing this community together through national and international collaborations, workshops and meetings which will optimise NERC and UK Government investment. Importantly, studentships are encouraged to visit and work with researchers involved in other national and international programmes in order to build future high quality capacity with early international experience. UK capacity in carbonate chemistry will be grown through the development of a multi-centred carbonate chemistry service.

11. Implementation Plan

The *Implementation Plan* for the *UK Ocean Acidification Research Programme* is available on the NERC website as a separate document and should be read prior to submitting a proposal.

12. References

Archer, D. and Brovkin, V., 2008. The millennial atmospheric lifetime of anthropogenic CO_2. *Climate Change* **90:** 283–297.

Avgoustidi V, 2006, Dimethyl production in the double-CO2 world, *PhD Thesis, Uni. East Anglia,* pp349.

Barcelos e Ramos, J., Biswas, H., Schulz, K.G., LaRoche, J. and Riebesell, U., 2007, Effect of rising atmospheric carbon dioxide on the marine nitrogen fixer Trichodesmium, *Global Biogeochem. Cycles* **21:** GB2028, doi:10.1029/2006GB002898.

Barker, S. and Elderfield, H., 2002. Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2, *Science* **297:** 833-836.

Beaugrand, G., Reid, P.C., Ibanez, F., Lindley, J.A. and Edwards, M., 2002. Reorganization of North Atlantic Marine Copepod Biodiversity and Climate, *Science* **296:** 1692-1694.

Bellerby R.G.J., Olsen A., Furevik T. and Anderson L.A., 2005. Response of the surface ocean CO2 system in the Nordic Seas and North Atlantic to climate change. In: *Climate Variability in the Nordic Seas* Drange, H., Dokken, T.M., Furevik, T., Gerdes, R. and Berger, W. (Eds.), *Geophysical Monograph Series* **158**: American Geophysical Union, Washington DC, 189-198.

Blackford, J.C. and Gilbert, F.J., 2007. pH variability and CO_2 induced acidification in the North Sea, *Journal of Marine Systems* **64:** 229–241.

Blackford J.C., Jones N., Proctor R. & Holt J., 2008. Regional scale impacts of distinct CO_2 additions, North Sea, *Marine Pollution Bulletin* **56**: 1461-1468.

Buckling, A., Wills, M.A. and Colegrave, N., 2003. Adaptation Limits Diversification of Experimental Bacterial Populations, *Science* **302**: 2107-2109.

Caldeira, K. and Wickett, M.E., 2003. Anthropogenic carbon and ocean pH, *Nature* **425:** 365.

DeBaar, H. http://www.scorint.org/High_CO2_II/Presentations/DeBaar.pdf

Delille, B., Harlay, J., Zondervan, I., Jacquet, S., Chou, L., Wollast, R., Bellerby, R.G.J., Frankignoulle, M., Borges, A.V., Riebesell, U., Gattuso, J-P., 2005. Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi*. *Global Biogeochemical Cycles* **19:** GB2023, doi:10.1029/2004GB002318.

Dickson, A.G., Sabine, C.L. and Christian, J.R., 2007. Guide to best practices for ocean CO2 measurements. ,Sidney, British Columbia. North Pacific Marine Science Organization (PICES Special Publication ,3)

Doney, S.C., Fabry, V.J., Feely, R.A. and Kleypas, J.A., 2009. Ocean Acidification: The Other CO_2 Problem, *Annual Review of Marine Science*, **1:** 169-192.

Dupont, S; Havenhand, J; Thorndyke, W, et al., 2008. Near-future level of CO2-driven ocean acidification radically affects larval survival and development in the brittlestar Ophiothrix fragilis. *Marine Ecology Progress Series* **373**: 285-294.

Dupont S. and Thorndyke M.C., 2009. Impact of CO_2-driven ocean acidification on invertebrates early life-history – What we know, what we need to know and what we can do, *Biogeosciences Discussions* **6:** 3109-3131.

Engel, A., Zondervan, I., Aerts, K., et al., 2005. Testing the direct effect of CO2 concentration on a bloom of the coccolithophorid *Emiliania huxleyi* in mesocosm experiments, *Limnol. Oceanogr.* **50:** 493-507.

Fabry V.J., Seibel B.A., Feely R.A. and Orr J.C., 2008. Impacts of ocean acidification on marine fauna and ecosystem processes, *ICES Journal of Marine Science* **65**: 414-432.

Feely, R.A., Sabine, C.L., Hernandez-Ayon, J.M., Ianson, D., Hales, B., 2008. Evidence for upwelling of corrosive 'acidified' water onto the continental shelf, *Science* **320:** 1490-1492, doi: 10.1126/science.1155676

Feng, Y., Warner, ME., Zhang, Y., et al., 2008. Interactive effects of increased pCO(2), temperature and irradiance on the marine coccolithophore *Emiliania huxleyi* (Prymnesiophyceae), *European Journal of Phycology* **43:** 87-98.

Findlay H.S., Wood H.L., Kendall M.A., Spicer J.I., Twitchett R.J. and Widdicombe S., 2009. Calcification, a physiological process to be considered in the context of the whole organism, *Biogeosciences Discussions* **6:** 2267-2284.

Gangsto R., Gehlen M., Schneider B., Bopp L., Aumont O. and Joos F., 2008. Modelling the marine aragonite cycle: changes under rising carbon dioxide and its role in shallow water CaCO3 dissolution, *Biogeosciences* **5:** 1057-1072.

Gazeau, F., Quiblier, C., Jansen, J.M., Gattuso, J-P., Middelburg, J.J. and Heip, C.H.R., 2007. Impact of elevated CO_2 on shellfish calcification, *Geophys. Res. Lett.*, **34:** L07603, doi:10.1029/2006GL028554.

Gibbs, S.J., Bown, P.R., Sessa, J.A., Bralower, T.J. and Wilson, P.A., 2006. Nannoplankton Extinction and Origination Across the Paleocene-Eocene Thermal Maximum, *Science* **314**: 1770-1773.

Guinotte, J.M., Orr, J., Cairns, S., Freiwald, A., Morgan, L. and George, R., 2006. Will human-induced changes in seawater chemistry alter the distribution of deep-sea scelaractinian corals? *Frontiers in Ecology and the Environment* **4 (3):** 141-146.

Hall-Spencer J.M., Rodolfo-Metalpa R., Martin S., Ransome E., Fine M., Turner S.M., Rowley S.J., Tedesco D. and Buia M.C., 2008. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification, *Nature* **454:** 96-99.

Hofmann, G.E, O'Donnell, M.J., Todgham, A.E, 2008. Using functional genomics to explore the effects of ocean acidification on calcifying marine organisms, *Marie Ecology Progress Series* **373:** 219–225.

Hopkins F.E., Turner S.M., Nightingale P.D., Steinke M. and Liss P.S., Ocean Acidification and Marine Trace Gas Emissions, *submitted to PNAS.*

Hutchins, D.A. et al., 2007. CO2 control of Trichodesmium N-2 fixation, photosynthesis, growth rates, and elemental ratios: Implications for past, present, and future ocean biogeochemistry. *Limnol. Oceanogr.* **52:** 1293-1304.

Iglesias-Rodriguez, M.D. et al., 2008. Phytoplankton calcification in a high-CO2 world, *Science* **320:** 336-340.

IOCCP (International Ocean Carbon Coordination Project), 2007. Surface Ocean CO_2 variability and vulnerabilities workshop. *IOCCP report 7*. UNESCO, Paris, France, 11-14. http://www.ioccp.org/

IPCC, 2007. Climate Change 2007: The physical science basis. Summary for policymakers. Contribution of working group I to the fourth assessment report. *The Intergovernmental Panel on Climate Change.*

Ishimatsu, A., Kikkawa, T., Hayashi, M., Lee, K., and Kita, J. 2004. Effects of CO_2 on marine fish: larvae and adults. *Journal of Oceanography*, **60:** 731–741.

Kelly, D.C., Bralower, T.J. and Zachos, J.C., 1998. Evolutionary consequences on the latest Paleocene

thermal maximum for tropical planktonic foraminifera, *Palaeogeography Palaeoclimatology Palaeoecology* **141**: 139-161.
Kleypas J. A., Feely R. A., Fabry V. J., Langdon C., Sabine C. L. and Robbins L. L., 2006. Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: *A Guide for Future Research* pp. 88, St. Pertsburg, Florida, USA.
Kurihara, H. & Ishimatsu A., 2008. Effects of high CO2 seawater on the copepod (*Acartia tsuensis*) through all life stages and subsequent generations, *Marine Pollution Bulletin*, **56**: 1086-1090.
Langer, G. et al., 2006. Species-specific responses of calcifying algae to changing seawater carbonate chemistry. *Geochemistry Geophysics Geosystems* **7:** Q09006, doi:10.1029/2005GC001227.
Larsen, B. K., Pörtner, H.O and Jensen, F.B, 1997. Extra and intracellular acid-base balance and ionic regulation in cod (Gadus morhua) during combined and isolated exposures to hypercapnia and copper. *Mar. Biol.* **128:** 337–346.
Le Quéré, C. Rodenbeck, C., Buitenhuis, E. T., Conway, T. J., Langenfelds, R., Gomez, A., Labuschagne, C., Ramonet, M., Nakazawa, T., Metzl, N., Gillett, N., Heimann, M., 2007. Saturation of the Southern Ocean CO_2 sink due to recent climate change. *Science* **316(5832):** 1735-1738.
Leonardos, N. and Geider, R.J., 2005. *J. Phycol.* **41**: 1196-1203.
Levitan, O. et al., 2007. Elevated CO2 enhances nitrogen fixation and growth in the marine cyanobacterium Trichodesmium, *Glob. Change Biol.* **13:** 531-538.
Marchitto, T.M., Curry, W.B. and Oppo, D.W., 2000. Zinc concentrations in benthic foraminifera reflect seawater chemistry, *Paleoceanography* **15**: 299-306.
Mayor, D.J., Matthews, C., Cook, K., Zuur, A.F. and Hay, S., 2007. CO2-induced acidification affects hatching success in *Calanus finmarchicus*. *Marine Ecology Progress Series* **350**: 91-97.
McNeil, B.I. and Matear, R.J., 2008. Southern Ocean acidification: A tipping point at 450-ppm atmospheric CO2, *Proceedings of the National Academy of Sciences* **105:** 18860-18864.
Millero, F.J., 1995. Thermodynamics of the carbon dioxide system in seawater, *Geochimica et Cosmochima Acta* **59 (4):** 661-677.
Moy, A.D., Howard, W.R., Bray, S.G & Trull, T.W., 2009. Reduced calcification in modern Southern Ocean planktonic foraminifera, *Nature Geoscience* doi:10.1038/NGEO460.
Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R.M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.G., Plattner, G.-K., Rodgers, K.B., Sabine, C.L., Sarmiento, J.L., Schlitzer, R., Slater, R.D., Totterdell, I.J., Weirig,M.-F., Yamanaka,Y. and Yool, A., 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms’, *Nature* **437(7059)**: 681–686.
Orr, J. C., Jutterstr ¨om, S., Bopp, L., Anderson, L. G., Fabry, V. J., Fr ¨ olicher, T. L., Jones, P.,Joos, F., Maier-Reimer, E., Segschneider, J., Steinacher, M., and Swingedouw, D: Arctic ocean acidification, *Nature*, submitted, 2008.
Orr, J.C., et al., 2009. Research Priorities for Ocean Acidification, report from the Second Symposium on the Ocean in a High-CO2 World, *Monaco, October 6-9, 2008, convened by SCOR, IOC-UNESCO, IAEA, and IGBP*, 23 pp.
Panchuk, K.M., Ridgwell, A. and Kump, L.R., 2008. Marine carbonate constraints on PETM carbon release in an earth system model, *Geology* **36**: 315-318.
Pörtner, H. O., Reipschläger, A. and Heisler, N., 1998. Metabolism and acid-base regulation in *Sipunculus nudus* as a function of ambient carbon dioxide, *J. Exp. Biol.*, **201:** 43–55.
Pörtner, H.O., Langenbuch M., Reipschlager, A., 2004b. Biological impact of elevated ocean CO_2 concentrations: Lessons from animal physiology and earth history, *J Oceanogr* **60:** 705–718.
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.
Pörtner H.O., Farrell A.P., Knust R., Lannig G., Mark F.C. and Storch D., 2009. Adapting to Climate Change Response, *Science* **323:** 876-877.
Rees, A.P., Dixon, J.L., Widdicombe, S., and Wyatt, N. Observations of nitrogen chemistry and fluxes under high CO_2 conditions: implications for the Mediterranean Sea. *CIESM Workshop Monograph* **No. 36 In Press**
Ridgwell, A. and Zeebe, R.E., 2005. The role of the global carbonate cycle in the regulation and evolution of the Earth system, *Earth and Planetary Science Letters* **234:** 299–315
Ridgwell, A., 2007. Interpreting transient carbonate compensation depth changes by marine sediment core modelling, *Paleoceanography* **22**: PA4102, http://dx.doi.org/4110.1029/2006PA001372
Ridgwell, A., Zondervan, I., Hargreaves, J., Bijma, J. and Lenton, T., 2007. Assessing the potential long-term increase of oceanic fossil fuel CO_2 uptake due to 'CO2-calcification feedback', *Biogeosciences* **4:** 481-492.
Ridgwell, A., Schmidt, D.N., Turley, C., Brownlee, C., Maldonado, M.T., Tortell, P. and Young, J.R., 2009. From laboratory manipulations to earth system models: predicting pelagic calcification and its consequences, *Biogeosciences Discuss.* **6:** 3455-3480
Riebesell U., Wolf-Gladrow, D. and Smetacek, V., 1993. Carbon-dioxide limitation of marine-phytoplankton growth-rates, *Nature* **361:** 249-250.
Riebesell, U. et al., 2000. Reduced calcification of marine plankton in response to increased atmospheric CO2, *Nature* **407 (6802):** 364-367.
Riebesell, U. et al., 2007. Enhanced biological carbon consumption in a high CO2 ocean. *Nature* **450:** 545-.
Riebesell, U. et al., 2008. Comment on "Phytoplankton Calcification in a High-CO_2 World", *Science* **322:** 1466
Rost, B. and Riebesell, U., 2004. Coccolithophore calcification and the biological pump: response to environmental changes. In: *Coccolithophores: from molecular processes to global impact.* H.R. Thierstein and J.R. Young (Eds), Springer, Berlin, pp. 99-126.
Rost B., Zondervan I. and Wolf-Gladrow D., 2008. Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. *Marine Ecology Progress Series.* **373:** 227-237.
Royal Society, 2005. Ocean acidification due to increasing atmospheric carbon dioxide. Policy document 12/05 *Royal Society, London.* The Clyvedon Press Ltd, Cardiff.
Royer, D.L., Berner, R.A., Montañez, I.P., Tabor, N.J. and Beerling, D.J., 2004. CO_2 as a primary driver of Phanerozoic climate, *GSA Today* **14:** 4- 10.
Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.-H., Kozyr, A., Ono, T. and Rios, A.F., 2004. The Oceanic Sink for Anthropogenic CO2, *Science* **305:** 367-371.
Schuster, U. and Watson, A.J.W., 2007. A variable and decreasing sink for atmospheric CO_2 in the North Atlantic. *Journal of Geophysical Research,* **112:** C11006, doi:10.1029/2006JC003941.
Sciandra, A; Harlay, J; Lefevre, D, et al., 2003. Response of coccolithophorid *Emiliania huxleyi* to elevated partial pressure of CO2 under nitrogen limitation. *Marine Ecology Progress Series* **261:**111-122.
Siegenthaler, U., Stocker, T.F., Monnin, E., Luthi, D., Schwander, J., Stauffer, B., Raynaud, D., Barnola, J.-M., Fischer, H., Masson-Delmotte, V. and Jouzel, J., 2005. Stable Carbon Cycle-Climate Relationship During the Late Pleistocene, *Science* **310**: 1313-1317.
Sluijs, A., Bowen, G.J., Brinkhuis, H., Lourens, L.J. and Thomas, E., 2007. The Palaeocene-Eocene Thermal Maximum super greenhouse: biotic and geochemical signatures, age models and mechanisms of global change. Williams, M., Haywood, A.M., Gregory, F.J. and Schmidt, D.N., (Eds), *Deep time perspectives on climate change - marrying the signal from computer models and biological*

proxies, TMS Special Publication 2, The Geological Society of London, London.
Steinacher, M., Joos, F., Frölicher, T.L., Plattner, G-K. and Doney, S.C., 2008. Imminent ocean acidification projected with the NCAR global coupled carbon cycle-climate model, *Biogeosciences Discuss*. **5**: 4353-4393
Thomas, E., 2007. Cenozoic mass extinctions in the deep sea: what perturbs the largest habitat on earth? *Large Ecosystem Perturbations: Causes and Consequences: Geological Society of America Special* Monechi, S., Coccioni, R. and Rampino, M.R., (Eds), **Paper 424**, 1-23.
Thomas H., Schiettecatte L.S., Suykens K., Koné Y. J. M., Shadwick E. H., Prowe A. E. F., Bozec Y., de Baar H. J. W., and Borges A. V., 2008. *Biogeosciences Discussions* **5**: 3575-3591.
Tortell, P.D. et al., 2008. Inorganic carbon uptake by Southern Ocean phytoplankton, *Limnol. Oceanogr.* **53:** 1266-1278.
Turley, C., Blackford, J., Widdicombe, S., Lowe, D., Nightingale, P.D. and Rees, A.P., 2006. Reviewing the impact of increased atmospheric CO2 on oceanic pH and the marine ecosystem. In: *Avoiding Dangerous Climate Change*, Schellnhuber, H J., Cramer,W., Nakicenovic, N., Wigley, T. and Yohe, G (Eds), Cambridge University Press, 8, 65-70.
Turley, C., Findlay, H.S., Mangi, S., Ridgwell, A. and Schmidt, D.N., 2009. MCCIP Ocean Acidification Review. http://www.mccip.org.uk/
Tyrrell, T., Schneider, B., Charalampopoulou, A., and U. Riebesell, U., 2008. Coccolithophores and calcite saturation state in the Baltic and Black Seas, *Biogeosciences* **5:** 485-494.
Vogt, M., Steinke, M., Turner, S., Paulino, A., Meyerhöfer, M., Riebesell, U., LeQuéré, C. and Liss, P., 2008. Dynamics of dimethylsulphoniopropionate and dimethylsulphide under different CO2 concentrations during a mesocosm experiment, *Biogeosciences* **5:** 407-419.
Widdicombe S. and Needham H.R., 2007. Impact of CO_2 induced seawater acidification on the burrowing activity of *Nereis virens* and sediment nutrient flux, *Marine Ecology Progress Series* **341:** 111-122.
Widdicombe, S. and Spicer, J.I., 2008. Predicting the impact of Ocean acidification on benthic biodiversity: What can physiology tell us? *Journal of Experimental Marine Biology and Ecology* **366:** 187-197.
Widdicombe S., Dashfield S.L., McNeill C.L., Needham H.R., Beesley A., McEvoy A., Øxnevad S., Clarke K.R. and Berge J.A., 2009a. Effects of CO_2 induced seawater acidification on infaunal diversity and sediment nutrient fluxes. *Marine Ecology Progress Series* **In press.**
Wood, H.L., Spicer J.I., and Widdicombe, S., 2008. Ocean acidification may increase calcification rates, but at a cost. *Proceedings of the Royal Society: B* **275:** 1767-1773.
Wood H.L., Widdicombe S. and Spicer J.I., 2009. The influence of hypercapnia and macrofauna on sediment nutrient flux – will ocean acidification affect nutrient exchange? *Biogeosciences Discussions* **6:** 2387-2413.
Yu, J. and Elderfield, H., 2007. Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, *Earth and Planetary Science Letters* **258:** 73-86.
Yu, J., Elderfield, H. and Hönisch, B., 2007. B/Ca in planktonic foraminifera as a proxy for surface seawater pH, *Paleoceanography* **22** PA2202, http://dx.doi.org/2210.1029/2006PA001347
Zachos, J.C., Pagani, M., Sloan, L., Thomas, E. and Billups, K., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present, *Science* **292:** 686-693.
Zachos, J.C., Kroon, D., Blum, P., Bowles, J., Gaillot, P., Hasegawa, T., Hathorne, E.C., Hodell, D.A., Kelly, D.C., Jung, J.-H., Keller, S.M., Lee, Y.S., Leuschner, D.C., Liu, Z., Lohmann, K.C., Lourens, L., Monechi, S., Nicolo, M., Raffi, I., Riesselman, C., Röhl, U., Schellenberg, S.A., Schmidt, D.N., Sluijs, A., Thomas, D.J., Thomas, E. and Vallius, H., (Eds), 2004. *Early Cenozoic extreme Climates: The Walvis Ridge transect, Ocean Drilling Program, College Station, TX.*
Zaric, S., Schulz, M. and Mulitza, S., 2005. Global prediction of planktic forminiferal fluxes from hydrographic and productivity data, *Biogeosciences Discussions* **2**: 849-895.
Zeebe, R.E. and Wolf-Gladrow, D., 2001. CO_2 in seawater: Equilibrium, kinetics, isotopes, Elsevier Oceanographic Series, Elsevier, New York.
Zeebe, R.E. and Zachos, J.C., 2007. Reversed deep-sea carbonate ion basin gradient during Paleocene-Eocene thermal maximum, *Paleoceanography* **22** PA3201, http://dx.doi.org/3210.1029/2006PA001395
Zondervan I., Rost B. and Riebesell U., 2002. Effect of CO2 concentration on the PIC/POC ratio in the coccolithophore *Emiliania huxleyi* grown under light-limiting conditions and different day lengths. *Journal of Experimental Marine Biology and Ecology* **272:** 55-70.

13. Glossary

ASH = Aragonite Saturation Horizon
BAS = British Antarctic Survey
BIOACID = Biological Impacts of Ocean ACIDification
DECC = Department of Energy and Climate Change
Defra = Department for Environment, Food and Rural Affairs
DIC = Dissolved Inorganic Carbon
DMS = Dimethyl Sulphide
DMSP = Dimethylsulphoniopropionate
EPOCA = European Project on Ocean Acidification
EU = European Union
HEI = Higher Education Institution
HNLC = High Nutrient Low Chlorophyll
IGBP = International Geosphere-Biosphere Programme
IPCC = Intergovernmental Panel on Climate Change (http://www.ipcc.ch/ipccreports/assessments-reports.htm)
KE = Knowledge Exchange
LWEC = Living With Environmental Change (http://www.nerc.ac.uk/research/programmes/lwec/)
MCCIP = Marine Climate Change Impacts Partnership (http://www.mccip.org.uk/arc/2007/default.htm)
MEECE = Marine Ecosystem Evolution in a Changing Environment (EU Project)
MSFD = Marine Strategy Framework Directive
NERC = Natural Environment Research Council

NOCS = National Oceanography Centre, Southampton
OA = Ocean Acidification
OVOCS = Oxygenated Volatile Organic Compounds
PML = Plymouth Marine Laboratory
RCUK = Research Councils United Kingdom
SAMS = The Scottish Association for Marine Science
SCOR = Scientific Committee on Oceanic Research
TA = Total Alkalinity
UNESCO = United Nations Educational, Scientific and Cultural Organisation
UNFCCC = United Nations Framework Convention on Climate Change
VICS = Volatile Iodine Compounds
WGBU = Scientific Advisory Board for the German Government for Climate change

14. Annex 1: BIOACID

Please see the separate document on the NERC website for details of BIOACID.

15. Annex 2: EPOCA and MEECE Summaries and contacts

The ocean helps moderate climate change thanks to its considerable capacity to store CO_2, through the combined actions of ocean physics, chemistry, and biology. This storage limits the amount of human-released CO_2 remaining in the atmosphere. As CO_2 reacts with seawater, it generates dramatic changes in carbonate chemistry, including decreases in *p*H and carbonate ions and an increase in bicarbonate ions. The consequences of this overall process, known as "ocean acidification", are raising concerns for its biological, ecological, biogeochemical, and societal implications. The overall goal of the *European Project on Ocean Acidification* (EPOCA; epoca-project.eu) is to fill numerous gaps in the understanding of the consequences of ocean acidification. The EU funded project started in May 2008 and runs for 4 years. The Coordinator is Jean-Pierre Gattuso (gattuso@obs-vlfr.fr) and the Project Manager is Lina Hansson (hansson@obs-vlfr.fr), CNRS - Laboratoire d'Océanographie de Villefranche (France). The research interests of EPOCA are divided into four themes, each with a leader:

First, EPOCA aims to document the changes in ocean chemistry and geographical distribution of marine organisms across space and time. Paleo-reconstruction methods are used on several archives, including foraminifera and deep-sea corals, to determine the past variability in ocean chemistry (carbonate, nutrients and trace metals) and to tie these to present-day chemical and biological observations. Theme Leader: Jella Bijma (Jelle.Bijma@awi.de).

Second, EPOCA devotes much effort to quantifying the impact of ocean acidification on marine organisms and ecosystems. Key climate-relevant biogeochemical processes such as calcification, primary production and nitrogen fixation are investigated using a large array of techniques, ranging from molecular tools to physiological and ecological approaches. Perturbation experiments are carried out both in the laboratory and in the field. Key organisms are selected on the basis of their ecological, biogeochemical or socio-economic importance. Theme Leader: Ulf Riebesell (uriebesell@ifm-geomar.de).

Third, the modelling component of EPOCA integrates the chemical, biological and biogeochemical impacts of ocean acidification into biogeochemical, sediment and coupled climate carbon cycle models. Special attention is paid to feedbacks of physiological changes on the carbon, nitrogen, sulphur and iron cycles and in turn how these changes will affect and be affected by future climate change. Theme Leader: Marion Gehlen (Marion.Gehlen@cea.fr).

Finally, EPOCA assesses uncertainties, risks and thresholds ("tipping points") related to ocean acidification at molecular, cellular, organismal, local and global scales. It also assesses pathways of CO_2 emissions required to avoid the identified thresholds and describe the state change if these emissions are exceeded and the subsequent risk to the marine environment and Earth system. Theme Leader: Carol Turley (ct@pml.ac.uk)

MEECE
Marine Ecosystem Evolution in a Changing Environment

MEECE is a European FP7 Integrated Project which aims to increase ecosystem modelling predictive capacities. Both natural and human-induced climate pressures have an impact on the structure and function of marine ecosystems. Using a combination of data synthesis, numerical simulation and targeted experiments MEECE intends to boost our knowledge and develop the predictive capabilities needed to learn about the response of marine ecosystems.

MEECE will also develop methods to integrate the dynamic response of marine ecosystems to the combined effects of various anthropogenic and natural drivers in order to provide decision making tools to support the EC Marine Strategy, EC Maritime Policy and the EC Common Fisheries Policy.

The MEECE Project Coordinator is Icarus Allen (JIA@pml.ac.uk.). There are 6 main workpackages (WP) within the MEECE project. Below are the WP titles and leaders but please see the MEECE web site: http://www.meece.eu/ for individual descriptions and further details:

WP1: Driver Parameterisations and model scenarios - Richard Bellerby and Sergej Olenin

WP2: Advanced modelling - Mike St John and Steve Mackinson

WP3: Ecosystem response to climate change and acidification - Xabier Irigoien and Jason Holt

WP4: Ecosystem response to direct anthropogenic drivers - Marco Zavatarelli and Yunne Shin

WP5: Implications for resource management - GerJan Piet and Fritz Köster

WP6: Knowledge Transfer and Outreach - Manuel Barange and Jessica Heard