THE NERC MARINE CENTRES' STRATEGIC RESEARCH PROGRAMME 2007-2012

# Theme 2: Marine Biogeochemical Cycles

Very small organisms in the ocean have big effects on the planet, influencing atmospheric composition and the global cycles of many elements. This Theme will study the role of marine phytoplankton and other microbes in relation to biogenic gas production and the flux of material to the deep ocean. It includes nutrient cycling, biophysical interactions and rate-limiting physiological processes, with the overall aim of improving predictions of how marine biogeochemical cycles will respond to global change, including ocean acidification.

Theme 2 comprises three Research Units and ten Work Packages:

**Marine biogeochemical cycles in a high $CO_2$ world (Plymouth Marine Laboratory).**
*PML Theme Leader: Phil Nightingale pdn@pml.ac.uk*

WP 2.1 Improved quantification of the carbon cycle in the surface ocean and shelf seas
WP 2.2 Reducing uncertainties in the microbial cycling of the major elements
WP 2.3 Quantifying the impact of a high $CO_2$ world on marine biogeochemical cycles and feedbacks
WP 2.4 Links between photophysiology, stress responses and biogenic gas production

**The ocean's biological carbon pump and its sensitivity to climate change (National Oceanography Centre, Southampton).** *NOCS Theme Leader: Dave Billett d.billett@noc.soton.ac.uk*

WP 2.5 Physical processes and the supply of nutrients to the photic zone
WP 2.6 Plankton communities and biogeochemistry
WP 2.7 Export into the ocean's interior

**Cellular and molecular responses of calcification to rapid climate change (Marine Biological Association).** *MBA Theme Leader: Colin Brownlee cbr@mba.ac.uk*

WP 2.8 Cellular processes that underpin coccolithophore ecophysiology: impact of environmental change
WP 2.9 Molecular and cellular determinants of coccolithophore calcification: impact of elevated $CO_2$
WP 2.10 Community structure within coccolithophore blooms: effects of rapid environmental change

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# Theme 2: Marine Biogeochemical Cycles

### Strategic setting

Phytoplankton and other microbes in the ocean are crucial to the Earth system. They are currently slowing the pace of climate change by their net uptake of $CO_2$ that humans are adding to the atmosphere; they can also release other gases (such as dimethyl sulphide) with significant effects on climate. There is urgent need to know how such processes will change in the next 20-50 years. Whilst it seems inevitable that rising concentrations of atmospheric $CO_2$ will result in the ocean becoming both warmer and more acidic, we do not know how the marine biota that drive air-sea gas exchanges (and hence global element cycles) will respond to these changes – affecting key feedback systems, that may either amplify or mitigate the seriousness of future global warming.

This Theme addresses the impact of increasing atmospheric $CO_2$ on marine biogeochemical cycles. Researchers at PML, NOC and MBA will investigate the impact of expected changes in temperature, stratification, storminess and acidification, and identify the most sensitive processes in the microbial cycling of carbon, nitrogen, sulphur and iodine. The aim is to predict how altered marine biogeochemical cycles will respond through changes in magnitude, and possibly in direction, of fluxes of climate-active gases, and in the efficiency of the biological pump. In order to make reliable predictions, we need better knowledge of present day biogeochemical cycles – the key processes that control the cycling of climate active gases within the surface ocean; the main transport mechanisms governing the supply of nutrients from deeper waters across the pycnocline; and the flux of material to deep water via the biological carbon pump. These processes will be quantified by a combination of observations, experiments and modelling, leading to improved predictions of the impact of high $CO_2$ on the surface ocean.

The biogeochemistry of the surface ocean and its interactions with both the atmosphere and the deep ocean are central to Oceans 2025 and to NERC's current strategic priorities, of Earth's Life Support Systems and Climate Change (NERC, 2002). The research topics encompassed by Theme 2 are also highly relevant to Defra policy on 'Climate Change and Energy'. The information and advances in understanding and predictive capability that we will make will be used elsewhere in NERC (e.g. BAS, CASIX, UK SOLAS, QUEST and NCAS); by national bodies such as NCOF and the Hadley Centre; and will contribute to international assessments (IPCC) and policy formulation. Ocean biogeochemical cycles and their climate feedbacks have been identified as of very high priority by the international research programmes, SOLAS and IMBER, and by the Earth System Science Partnership of SCOR, WCRP, IGBP, DIVERSITAS and CAGCP.

### Theme-wide science aims

The broad aim of this Theme is to improve knowledge of major biogeochemical processes in the surface layer of the Atlantic Ocean and UK shelf seas in order to develop accurate models of these systems. This strategic research will result in predictions of how the ocean will respond to, and either ameliorate or worsen, climate change and ocean acidification. Pivotal biogeochemical pathways and processes include the following, identifying the main Centres involved:

- The oceans and shelf seas as a source and sink of climate active gases (PML)
- The importance of the carbon and nitrogen cycles in the regulation of microbial communities and hence export (NOC) and biogenic gas cycling (PML)
- The biological pump and export of carbon into the ocean's interior (NOC).
- Processes that introduce nutrients into the euphotic zone (NOC)
- The direct impact of a high $CO_2$ world (acidification) on mixed layer biogeochemical cycles and feedbacks to the atmosphere via sea/air gas fluxes (PML) and the biological pump (NOC)
- The indirect impact of a high $CO_2$ world (increased stratification and storminess) on the supply of nutrients to the surface layer of the ocean and hence on the biological carbon pump (NOC) and air-sea gas fluxes (PML).

- Cellular processes that mediate calcification in coccolithophores and how these are impacted by environmental change with a focus on elevated $CO_2$ and ocean acidification (MBA)
- Inter- and intra-specific genetic diversity and inter-specific physiological plasticity in coccolithophores and the consequences of rapid environmental change (MBA).

### Centre contributions

The research proposed by the three contributing marine Centres (PML, NOC and MBA) uses the distinct and complementary expertise available at each. Bringing together these Research Units into a coordinated Theme will enable comparison of processes across a range of scales, with each Centre concentrating on different processes. PML will focus on biogeochemical cycles in relation to biogenic gas production in the shelf seas and North Atlantic; NOC will focus on the implications of change for the biological carbon pump; whilst MBA will investigate the physiology of key organisms in the marine carbon cycle. In addition to the research that will be done by each Centre to achieve its objectives (described in Work Packages 2.1 – 2.10 below), synergies will be enhanced by collaborations that will include joint cruises, by the modelling approaches outlined in Theme 9, and through links to almost all other Themes in Oceans 2025.

Theme 2 research at PML will focus on the ocean carbon cycle, its interactions with the nitrogen cycle, and the main factors controlling the cycling of biogenic gases in surface seawater. PML will investigate the impact of high $CO_2$, especially ocean acidification, on microbial cycles and biogenic gas production and removal. PML will also examine the mechanisms used by phytoplankton to cope with increased stress that occur in a changing environment, again with an emphasis on carbon and biogenic gas cycling.

NOC will concentrate on the open ocean and on the biological pump. In particular, NOC will examine physical mechanisms that re-supply nutrients to surface waters, phytoplankton community composition and export from the surface layer, with emphasis on exchanges between the surface mixed layer and deeper waters. NOC will quantify the sensitivity of the biological pump to changes in climate both directly, as a consequence of ocean stratification and acidification, and indirectly by changes in nutrient supply.

MBA will characterise mechanisms, regulation and adaptation of biogeochemical drivers and rate limiting processes that operate in coccolithophorid phytoplankton, a group of major ecological importance that may be particularly sensitive to global change. Attention will be paid to responses in the short term at the cellular level, and in the longer term at the population genetic level.

The research activities are highly complementary. For example, the impacts of acidification will be studied by MBA at the cellular and molecular level using laboratory cultures and analysis of natural populations obtained from cruise samples and preserved SAHFOS archives from the Continuous Plankton Recorder (SO 15); PML will investigate the pH sensitivity of calcified plankton as producers of climate active gases and possible long-term adaptation, using both mesocosm and microcosm experiments; whilst NOC will test the role of calcifiers as ballast agents that promote carbon export into the deep ocean using broad, basin-scale observations.

## Marine biogeochemical cycles and feedbacks in a high $CO_2$ world *Contribution to Theme 2 by Plymouth Marine Laboratory*

### Background

To date, the oceans have removed ~50% of the anthropogenic $CO_2$ released to the atmosphere (Sabine *et al*. 2004). They are also a source of climate-active gases (e.g. dimethyl sulphide, DMS) for which the sea to air flux represents a small loss from a much larger marine cycle (Archer *at al*., 2002). Sulphur compounds in the atmosphere change the quantity and quality of light reaching the surface ocean, affecting light-driven processes – photosynthesis and photochemistry – that are fundamental to biogeochemical cycles. The human-driven increase in atmospheric $CO_2$ will result in the oceans and shelf seas becoming both warmer (and hence increasingly stratified) and more

acidic (Caldeira & Wickett 2003). However, little is known about the possible impact of these changes on marine biogeochemical cycles and the related exchanges of climate-active gases across the air-sea interface. The aim of the PML research is to better understand the key processes controlling biogeochemical cycles in the surface oceans, to quantify how these cycles will be altered in a high $CO_2$ world, and to predict whether these impacts will feed back to the atmosphere.

In order to know how marine biogeochemical cycles will perform in the future, it is necessary to understand how they behave now. At basin and global scales, there are still large uncertainties in estimates of the most basic processes – such as the balance between photosynthesis and respiration. Those uncertainties can best be removed by integrated studies of biogeochemical cycles. PML will extend studies of the carbon and nitrogen cycles and resultant fluxes of biogenic gases. We will investigate the microbial communities that are responsible for the marine component of the interacting Earth system. Through experimentation and modelling, we will develop predictions of how the oceans will change in response to acidification and increased storminess brought on by climate change. Finally, we recognize that climate change is likely to result in stress on individual organisms. The mechanisms that enable phytoplankton to acclimate to changing environments are poorly understood: such responses need to be quantified for inclusion in ecosystem models.

## WP 2.1 (PML) Improved quantification of the carbon cycle in the surface ocean and shelf seas

**Specific objectives**

i) To determine the major controls on the variability in plankton respiration and photosynthesis including the photochemical alteration of microbial substrates.
ii) To determine the balance between microbial consumption and photochemical production of oxygenated volatile organic compounds (OVOCs).
iii) To quantify the role of the viral shunt in the cycling of carbon.

**Rationale**

The carbon cycle of the ocean is a key component of the Earth system. We need to know much more about how it is regulated by the 'microbial engine', driven by photosynthesisers (microalgae and cyanobacteria) and decomposers (bacteria, archaea and viruses). In particular, plankton respiration (R) has been described as the largest gap in our understanding of the ocean carbon cycle (Williams & del Giorgio 2005). The metabolic state of the ocean (production [P] minus [R]) is still ill defined; P/R ratios derived from instantaneous measurements of $O_2$ flux disagree on the sign of the balance, let alone the magnitude (Williams 1998). Comparison of global R and P data suggests that open ocean P has been severely underestimated (Robinson & Williams 2005), and that the best estimate of P is likely to be derived from a range of approaches (Marra 2002). The possibility that the episodic nature of P is poorly represented by bottle incubations has led to the idea that R may be a better predictor of P than P itself (Williams *et al*. 2004). Since global estimates of R integrate many aspects of ecosystem function, long term shifts in R may provide the best warning of change in ocean productivity processes. Photochemistry has a significant impact on carbon cycling by the degradation of coloured dissolved organic matter (CDOM). The photolysis of CDOM will increase the concentration of organic substrates and could increase bacterial production by as much as 40% (Benner & Biddanda 1998). Any photochemical consumption of $O_2$ will influence its saturation and hence the magnitude of air-sea flux; the limited data suggest that, in the surface oligotrophic ocean, photochemistry consumes the same order of magnitude of $O_2$ as R (Obernosterer *et al* 2001; 2005).

Although there has been a huge international research effort aimed at quantifying the air-sea flux of $CO_2$, the exchange of organic carbon between the atmosphere and ocean remains largely unquantified. Recent data suggest that the net flux of total organic carbon may be greater than that of $CO_2$ and may explain observations of net heterotrophy in the NE Atlantic (Dachs *et al*. 2005). It has been proposed that a combination of the air-sea flux of oxidised volatile organic compounds

(OVOCs), and in particular methanol, together with *in situ* photochemical production from CDOM, could sustain methylotrophic organisms throughout the surface ocean (Heikes *et al*. 2002).

Viruses act as catalysts for biogeochemical cycles by transforming living plankton cells into dissolved material (Suttle 2005). This process is poorly quantified, but it is possible that up to 25% of photosynthetically-fixed carbon in the ocean is 'shunted' by viruses daily (Wilhelm & Suttle 1999). This pathway short-circuits the flow of carbon and nutrients to higher trophic levels by shunting it to the DOM pool. One result of this is enhanced respiration. Future ecosystem models will require quantification of the physiological response to virus infection, of rates of infection, and information on the organic metabolites that are released by virus infection (Gobler *et al* 1997).

**Approach and methodologies**

To address the global lack of measurements of R, the uncertainty in P and the impact of CDOM photochemical degradation, we will make concurrent measurements at a range of time and space scales. P and R will be derived from dissolved $O_2$ during light/dark incubations (Robinson *et al*., 2002). Primary productivity will be derived from short term photosynthetron $^{14}C$ incubations (Tilstone *et al*., 2003) and from *in situ* fast repetition rate fluorometry (FRRF) (Smyth *et al*., 2004). CDOM measurements will be made as outlined in Blondeau-Patissier *et al*. (2004). Photobleaching of CDOM and photochemical consumption of $O_2$ will be determined from *in situ* incubations using quartz bottles (Obernosterer *et al*., 2001). Concurrent measurements of plankton community structure, bio-optics, $pCO_2$, $O_2$, and inorganic nutrients will be used to interpret the comparisons between the three measures of P and the variability in R using multivariate statistics. Surface water $Ar/O_2$ ratios will be measured using membrane inlet mass spectrometry (Kaiser *et al*., 2005) funded via AMT (SO 1), enabling a comparison between net community production (NCP = P-R) derived from short term incubations and NCP derived from larger time and space scale $O_2$ fluxes. Measurements will be made on common samples collected over one annual cycle at the Western Channel Observatory (WCO, SO 10), two AMT cruises and Process Cruise 1. This level of sampling is required to understand the relevant spatial and temporal scales. Previous coastal temporal (e.g. Robinson *et al.* 1999, Duarte *et al*. 2004) and open ocean spatial studies (e.g. Robinson & Williams 1999; Robinson *et al*. 2002, Serrett *et al*. 2002) have revealed both net heterotrophic and net autotrophic annual balances and a variety of positive correlations between R, P, day length, temperature and community composition (Robinson *et al.* 2002b).

We will examine whether OVOCs, in particular methanol, represent a significant source of labile carbon for marine bacteria, and whether volatile organic carbon contributes to observations of net hetero-trophy. We will test the hypothesis that a combination of the air-to-sea flux of methanol together with *in situ* production from photochemical degradation of CDOM could sustain methylotrophic organisms throughout the surface ocean. Samples will be collected over an annual cycle at WCO (SO 10), on two AMT transects and on Process Cruises 1 and 2. Air and water OVOC measure-ments will be made by gas chromatography and production rates will be derived from irradiance and UV incubation experiments whilst consumption rates will be determined using radiotracers.

In order to characterise and quantify the role of the viral shunt in carbon cycling, we need to understand physiological responses to infection, rates of infection and the flux of organic metabolites and pigment alteration products that arise from infection. Development and assessment of virus productivity methodology will be central to obtaining accurate shunt rates to include in predictive models. Data will be obtained from two AMT cruises, Process Cruise 1 and over an annual cycle at WCO (SO 10). Laboratory experiments will also be undertaken to assess pathways and identify signatures of viral lysis by linking analytical chemistry with genomic approaches (transcriptomics and proteomics). This will help to identify the molecular basis and regulation of metabolite production and quantify organic matter conversion rates.

Results from all three studies will feed into models of biogeochemical processes that will be developed in Theme 9.

## WP 2.2 (PML) Reducing uncertainties in the microbial cycling of the major elements

**Specific objectives**

i) To identify the bacterioplankton responsible for the cleavage of DMSP to DMS and the consumption of DMS in natural waters, quantify rates and what controls these rates.
ii) To quantify the contribution of bacteria and viruses to the cycling of halocarbons
iii) To elucidate rates of new and regenerated nitrogen production, their role in nutrient stoichiometry and hence trace gas production
iv) To identify the limiting and co-limiting factors for the microbial cycling of carbon and nitrogen.

**Rationale**

Microbial diversity in the ocean is known to be high, suggesting that there should always be organisms present with the capacity to react to rapid environmental change, and exploit new environmental niches. However, we know little about the microbes that are responsible for the consumption and production of key biogeochemical compounds or how their activity affects the cycling of nutrients and climate-active biogenic gases. The aim is to reduce uncertainties in the key processes associated with the cycling of sulphur, iodine, bromine and nitrogen.

Studies on the pathways of dimethylsulphoniopropionate (DMSP) transformation to DMS have taught us much about the fate of primary production and how volatile, labile compounds are processed once in the dissolved phase (e.g. Archer *et al.,* 2002). One of the key controls of DMSP transformation is bacterial metabolism. It is hypothesised that sulphur demand for protein synthesis determines whether bacteria use DMSP for protein synthesis, so diverting sulphur from DMS production, or cleave DMSP to DMS, possibly using the acrylate as a carbon source (Kiene *et al*., 2000). Bacterial metabolism is also often the dominant sink of DMS itself. There is expanding information on which bacteria assimilate DMSP for protein metabolism (Malmstrom *et al.,* 2004), but little is known about the bacteria that cleave DMSP to DMS or those that metabolise DMS.

Despite their importance in atmospheric composition and climate change, the oceanic sources and sinks of many volatile halocarbon compounds remain unclear (Salawitch 2000). Although photochemical production mechanisms for volatile iodocarbons (VICs) have been identified, (Richter & Wallace, 2004), we know little about the relative importance of biological sources or sinks (Nightingale & Liss, 2003). Bacterial metabolism may act as a source of these gases through methylation of iodide (Amachi *et al*., 2004) or as a sink through utilisation of volatile iodocarbons as sources of carbon. We know even less about the mechanisms controlling the concentrations of volatile bromine compounds, and whether or not viral infection may be involved.

Understanding of new production has changed in recent years (Lipschultz *et al.* 2002) and there is need for data to update ecosystem models of oceanic microbial nitrogen cycling. DON is a significant nitrogen pool in surface seawater. However, the fluxes are poorly understood and bioavailability is largely unknown (Zehr & Ward 2002), even though regenerated nutrients contribute significantly to phytoplankton productivity and hence the cycling of biogenic gases in surface waters. There is ongoing debate about which single or combination of macro- and micro-nutrients is limiting biological productivity (e.g. Boyd *et al* 2000; Mills *et al*., 2004, Thingstad *et al*., 2005) and hence $CO_2$ drawdown (Cooper *et al*., 1996, Bakker *et al.,* 2005), biogenic gas cycling (Turner *et al*., 2004) and air-sea fluxes (Nightingale *et al*., 2000a). Additionally, the low availability of some essential trace elements can, in parts of the ocean, control the rate of photosynthesis, nitrogen cycling (Morel & Price, 2003) and trace gas fluxes.

**Approach and methodologies**

We will use a combination of $^{14}C$ and $^{35}S$ radiotracer experiments linked to flow cytometric sorting and FISH analysis to identify the bacteria that utilise DMSP either for protein synthesis and/or cleave it to DMS and acrylate. The role of viruses in shunting S-metabolites through the microbial loop will be assessed. This work will initially be conducted at WCO (SO 10) and on open ocean

cruises (e.g. AMT, Process Cruises 1 and 2) in waters with contrasting DMSP and DMS availability and in relation to estimates of bacterial production and protein synthesis/sulphur demand. The work will elucidate the functional taxonomy of bacteria and the controls on those functions related to a potentially crucial climate-relevant biogeochemical pathway.

We will use a combination of radiotracer and natural isotope addition experiments to investigate the rates of: a) transformation of methyl donor compounds e.g. S-adenosyl-L- methionine to VICs; b) oxidation of labelled VICs; and c) virus lysis that increase VIC production. This work will start with cultures but will later include a study of the seasonal cycle of VICs, building on work already conducted at L4 (July 2002 - April 2004; Archer *et al.* submitted). We will also investigate oceanic waters during Process Cruises 1 and 2, where different processes are likely to be involved in VIC cycling. The information will be used to improve parameterisation of an ecosystem model that incorporates VIC cycling and is a logical extension to our new DMS/DMSP ecosystem model (Archer *et al.* 2004).

We will build on our on-going work on the distribution and activity of nitrogen fixation (Rees *et al*., 2006a) and nitrification organisms (Rees *et al* 2006b) and the bioavailability of DON in order to define their relative contributions to nitrogen turnover (Rees *et al*., 2002). Methods for this work will include molecular techniques and both stable (Clark *et al*., 2005) and radio-isotopes (Joint *et al*., 2001) over an annual cycle at WCO, during two AMT cruises and Process Cruises 1 and 2. We will use our experimentally-derived observations to refine.estimates and models of the upper ocean nitrogen cycle. This will be forced on regional scales using remotely sensed observations of chlorophyll and temperature, and will ultimately be used to improve estimates of new production and their impact on marine biogeochemical cycles.

We will investigate the influence of combinations of nutrients and the trace elements zinc and cobalt in controlling carbon and nitrogen cycling in the euphotic zone and hence the sea-to-air flux of biogenic gases. Incubation experiments will be conducted, and rate processes (e.g. carbon fixation, nitrification, bacterial production and biogenic gas production) determined during Process Cruises 1 and 2 planned for the period of Oceans 2025. These results will refine our under-standing of nutrient and trace element limitation of biological productivity, nitrogen cycling and trace gas production in nutrient-poor waters.

## WP 2.3 (PML) Quantifying the impact of a high $CO_2$ world on marine biogeochemical cycles and feedbacks

### Specific objectives

i) To evaluate the capacity of marine microbes to adapt to change.
ii) To determine the impact of high $CO_2$ on nutrient availability and microbial activity
iii) To evaluate the impact of ocean acidification on the air-sea transfer of biogenic gases
iv) To predict how changes in storm frequency and stratification impact air-sea gas transfers.

### Rationale

Atmospheric $CO_2$ influences marine ecosystems directly as dissolved $CO_2$ and indirectly through climate change. Increased $CO_2$ concentrations are likely to have variable effects on different marine phytoplankton species because of differences in their efficiency of carbon acquisition and their ability to regulate $CO_2$ concentration as a function of $CO_2$ supply (Rost *et al*., 2003, Tortell, 2000). In the long term, natural selection in a high $CO_2$ world is likely to increase the abundance of genotypes with ‘advantageous’ phenotypic features.

The most important effect of increased dissolved $CO_2$ is probably a reduction in pH (Caldeira & Wickett 2003) although a reduction in carbonate ions may also be relevant (Riebesell *et al*., 2000). The impact of lower pH on marine ecosystems is uncertain, but it is likely to change community structure and hence biogeochemical cycles (Raven *et al.*, 2005). Nothing is known about how the

viral shunt will react to increased temperature and/or $CO_2$, although there may be dramatic changes in the infection strategy of viruses infecting calcifying phytoplankton in a more acidic ocean.

Although the ocean has removed ~50% of the anthropogenic $CO_2$ released to the atmosphere (Sabine *et al*., 2004), the annual uptake is only 2% of the total $CO_2$ flux exchanged between atmosphere and ocean, and a much smaller fraction of the total carbon cycled in marine ecosystems. Nevertheless, the oceanic pH change anticipated within a century will have unknown consequences for biogeochemical cycles. We have already observed a halving of DMS levels in seawater at high $CO_2$ during mesocosm experiments to investigate the impact of doubled atmospheric $CO_2$. If such changes in DMS occurred throughout the ocean, they could result in an increase in global temperatures of ~2°C (Avgoustidi *et al*., submitted).

Global warming is expected to lead to enhanced water column stratification but the consequences are not clear. Stronger stratification could lead to a decrease in the supply of new nutrients to the surface ocean and ultimately a reduction in plankton stocks (Schmittner, 2005). Conversely, the strength and occurrence of episodic extreme weather events is expected to increase. This may reduce productivity in the short term through deep mixing, but could also introduce nutrients to surface waters that may enhance longer term productivity (Zhang *et al.,* 2001). Storms should increase sea-to-air gas transfer rates but enhanced stratification will limit exchange (Nightingale *et al.*, 2000). However, expected changes in source or sink strengths may have a greater impact on air-sea gas fluxes. Stratification of upper waters may increase surface concentrations of photochemically-produced gases (e.g. VICs) enhancing sea-to-air transfer whilst a greater occurrence of upper ocean oxygen minima would favour the production of $N_2O$ through both nitrification and denitrification (Codispoti *et al*., 2001) and $CH_4$ due to changes in the balance between methanogenesis and methane oxidation (Law, 2001).

**Approach and methodologies**

We will carry out longterm (months to years) culture experiments of representative marine phytoplankton species and monitor changes in a range of physiological parameters, e.g. growth rates and carbon concentrating mechanism efficiency, throughout the experimental period to examine the effects of increasing $pCO_2$ on these primary producers. We will quantify the gene expression of key enzymes involved in $CO_2$ assimilation (Wawrik *et al*., 2002) at representative time points during the period of culture in order to detect cells with altered genotypes.

The impact of high $CO_2$ on nutrient speciation and availability, and hence on phytoplankton, bacteria and virus activity, will be tested using a combination of dedicated enclosure experiments (mesocosms and incubations during cruises) and laboratory based experiments using samples derived from the WCO (SO 10). Measurements of changes in photosynthesis, respiration and CDOM photo-oxidation will be made to better understand the impact of acidification on the microbial cycling of carbon and to improve model predictions. The downstream effects of any changes on oceanic biogeochemical cycling will be assessed using these results in combination with conceptual models as well as the 1D and 3D models developed in Themes 6 and 9.

We will determine the impacts of changes in pH and temperature on the cycling of biogenic gases in seawater and the magnitude of changes in the sea-to-air flux of biogenic gases. We will use the results from investigations into key process rates described above, with improved 1D and 3D models (Themes 6 and 9) and with data obtained from the laboratory and mesocosm experiments to examine how changes in ecosystems impact on the cycling of the climate active gases such as DMS, volatile halocarbons, $N_2O$ and $CH_4$.

The impact on seasonal cycle evolution will be quantified to determine the effects of reduced winter mixing versus increased intermittent mixing episodes during summer. Scenario simulations with idealised forcing will provide information on the impacts of winter versus summer mixing anomalies on the evolution of the pelagic/benthic ecosystem. We will improve vertical mixing estimates under contrasting environmental conditions using data assimilation and 1D modelling of Lagrangian tracer releases (e.g. Law *et al*., 2003) and detailed nutrient profiles through the

pycnocline. We will use observations, together with 1D and 3D models, to predict the impact of changes in mixing on the sea-to-air flux of climate relevant gases (e.g. DMS, halocarbons). We will determine $N_2O$ and $CH_4$ concentrations and air-sea fluxes under seasonally varying conditions over a seasonal cycle at SO 10 and in the two PML Process Cruises. *In situ* observations will be combined with experimental rate measurements under varying $O_2$ concentrations to develop conceptual models. Finally, we will investigate if there are synergistic effects of temperature and pH change. The results from individual process studies will be enhanced using 1D and 3D ecosystem models developed in Themes 6 and 9 and ecosystem information derived in Theme 3.

## WP 2.4 (PML) Links between photophysiology, stress responses and biogenic gas production

**Specific objectives**

i) To understand regulation of photophysiological response to stress at the transcription level
ii) To understand regulation of anti-oxidant mechanisms that generate climate-active gases
iii) To determine the consequences for DMS production of the anti-oxidant roles of glutathione and DMSP in phytoplankton.
iv) To evaluate how anti-oxidant systems respond to and impact on a changing redox environment

**Rationale**

The surface ocean experiences a highly dynamic light environment, affected by turbulence, weather patterns and seasons. To predict how phytoplankton will respond to future climate change, we need a better understanding of the mechanisms that they use to deal with stress. In response to pathogens, and a variety of other environmental stresses (e.g. high light, UV, low temperature and nutrient limitation), plant and algal photosynthetic systems produce a range of potentially-damaging reactive oxygen species (ROS), including superoxide, hydrogen peroxide $H_2O_2$ and the hydroxyl radical (Palenik *et al*., 1987). Phytoplankton depend on a variety of adaptable protective mechanisms to maintain photosynthetic capacity in the face of elevated ROS production (e.g. Sigaud-Kutner *et al.,* 2005). In doing so, they contribute to the redox chemistry of their environment through the release of reactive chemical radicals. How phytoplankton cells alter their photophysiology in response to stress has profound implications for photosynthetic efficiency and biogeochemistry.

**Approach and methodologies**

A novel combination of transcriptional and photo-physiological profiling will be used to study the photosynthetic response to stress in phytoplankton. Viral infection of *Emiliania huxleyi* will be used as the 'model' stress response (Wilson *et al*., 2005). Microarrays fabricated with probes derived from the *E. huxleyi* EST library, *E. huxleyi* virus strain 86 oligonucleotides and *E. huxleyi* chloroplast gene oligonucleotides will be used to profile the transcriptional response during the early stage of infection (Lindell *et al*., 2005). Photo-physiological profiling (FRRF) will link changes in photosynthetic efficiency to observed transcriptional changes. This approach will be applied to understand the regulation of photophysiological, including oxidative stress, responses to changing light, nutrient availability and temperature.

Haloperoxidase enzyme activity may behave as an oxidative stress response, reducing $H_2O_2$ levels by oxidizing halide ions and producing volatile halocarbons (Theiler *et al*., 1978). Transcriptional regulation of haloperoxidase enzyme activity will be determined using real-time polymerised chain reactions (PCR) to study the response of phytoplankton to oxidative stress at a molecular level and the consequences for volatile halocarbon production in the surface ocean. Similarly, DMSP lyase plays a key part in the hypothesized DMSP/DMS/DMSO antioxidant cascade (Sunda *et al*., 2002). Characterisation of DMSP lyase at the molecular level will improve understanding of the regulation and activity of this enzyme. The limited information on protein composition for DMSP lyase (e.g. Nishiguchi & Goff, 1995) will be investigated and available genome databases will be mined (e.g. *E. huxleyi*) to obtain relevant nucleotide sequences. Primers will be designed and used to amplify

and characterize DMSP lyase at the genomic and transcriptional levels; the protein sequence and conformation will also be examined.

Glutathione (GSH) has a number of functions in higher plants, including detoxification of ROS. Initial studies indicate that GSH concentrations in phytoplankton are similar to those found in higher plants and vary with light, UV exposure and nutrient limitation, consistent with an anti-oxidant function. GSH synthesis may divert assimilated sulphur away from DMSP synthesis and hence, DMS production. The factors that control whether assimilated sulphur is used for GSH synthesis or for an alternative, potential anti-oxidant in DMSP, will be examined in controlled laboratory culture and field studies. Radiotracers will be used to determine the synthesis and turnover rates of GSH and DMSP. Sulphur assimilation and synthesis of GSH (Wheeler *et al.*, 2003), rather than DMSP, will be examined in laboratory cultures, at SO 10 and on cruises.

Studies in higher plants indicate chlorophyll catabolism is a highly regulated pathway yielding non-photochemically active compounds (Eckardt *et al.*, 2004). Preliminary work has shown similar compounds to be present in algal cultures (PML unpublished data). Chlorophyll catabolism may be important in reducing ROS production when phytoplankton are exposed to stress. We will investigate the production of chlorophyll catabolites during oxidative stress using two model systems: virus infection and light stress. The dynamics of photoprotective and antioxidant systems (GSH, DMSP, chlorophyll catabolites, carotenoids, mycosporine-like amino acids) will be compared in relation to environmental stress, including variations in extracellular peroxide concentrations. The study will be extended to natural phytoplankton communities at the WCO (SO 10). This work will contribute to our understanding of the fate of key photosynthetic constituents of phytoplankton during environmental stress.

**Summary research plan and deliverables for WP 2.1 – 2.4**

| | |
|---|---|
| 2007 | • pH manipulation studies in Bergen mesocosm |
| 2007-11 | • Studies using laboratory cultures<br>• Laboratory incubation/manipulation experiments with WCO water<br>• Microcosm work at PML using cultures and/or field samples |
| 2008 | • Process Cruises 1 and 2, part-funded by UK SOLAS |
| 2009 | • Coordinated seasonal cycle at WCO |
| 2010 -11 | • Two enhanced AMT cruises between UK and Falklands |

Main deliverables:

- Improvement in predicting the impact of a high $CO_2$ world on marine biogeochemical cycles
- Assessment of major controls on the variability of upper ocean production and respiration, and of the contribution of CDOM photodegradation to production, $O_2$ and OVOC fluxes
- Quantification of the air-sea flux of OVOCs and bacterial cycling of climate active gases (VICs, DMS, OVOCs)
- Evaluation of the role of viral shunt in the carbon cycle
- Incorporation of N fixation and nitrification rates into new production estimates and refined regional estimates of new production
- Identification of the regulatory mechanisms governing the photo-physiological response to environmental stress in phytoplankton
- Quantification of the contribution of anti-oxidant systems to biogeochemical flux of S, N, C and I, including biogenic gas production
- Evaluation of the impact of climate change on ocean feedbacks to the atmosphere by identifying key pathways and producing data to validate process models (with Themes 6 and 9).

# The ocean's biological carbon pump and its sensitivity to climate change

*Contribution to Theme 2 by the National Oceanography Centre, Southampton*

**Background**

The ocean's biological carbon pump (OBP) is an important process in the global carbon cycle. Small changes in its magnitude resulting from climate change could have significant effects both on the ocean's ability to sequester $CO_2$ and on the natural flux of marine carbon. We propose an integrated, multidisciplinary programme to understand the OBP, evaluate OBP processes that are climatically sensitive and model the sensitivity of the OBP to climate change.

Human activities are remobilising massive quantities of carbon from fixed reserves into the atmosphere with consequences for our climate. Currently, the rate of atmospheric increase in $CO_2$ is much slowed by the large net flux to the ocean, of around 1.5 – 2.0 billion tonnes C $yr^{-1}$. Within the ocean, two pumps are responsible for moving that carbon downwards, away from surface waters: the solubility pump and the OBP. While the former is directly dependent on upper ocean temperature and enhanced atmospheric $CO_2$, and can therefore be relatively easily modelled (Theme 1), the OBP involves complex biological processes that are non-linear - and hence difficult to understand and model. Furthermore, many processes involved in the OBP are likely to be sensitive to climate change.

The starting point for the OBP is when phytoplankton in sunlit waters convert inorganic carbon, dissolved in seawater, to an organic form inside their cells. This process causes a relative deficiency of dissolved carbon in the water near the sea surface – and hence a net uptake of atmospheric $CO_2$. The nature and activity of the algal community are strongly influenced by light and nutrients (N, P, Si, Fe), and the climatically-sensitive supply of these nutrients via ocean physics. Subsequent stages of the OBP transport around 20% of the total oceanic primary production of ~40-50 Gt C $yr^{-1}$ (IPCC, 2001) down below the seasonal thermocline where it remains out of contact with surface waters for periods ranging from years to centuries. Hence even small, climate-mediated changes in circulation and primary production could substantially change the role of the ocean in the global carbon cycle. A much more explicit understanding of the current OBP activity is needed if we are to evaluate and model ocean carbon dynamics in the future.

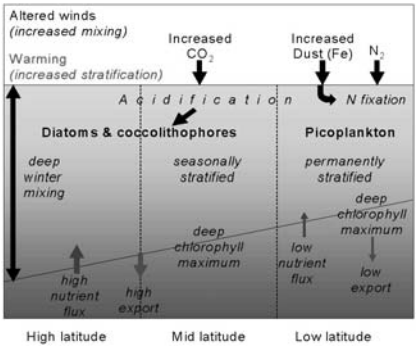


**Figure 1**. Simplified cartoon of climatically sensitive environmental forcing (arrows) and impact on the BP. The BP comprise the phytoplankton community (of which key taxa are shown) and the processes that influence its export into deep water. The left panel show the BP impacted by changed physics and $CO_2$ in the subpolar gyre at OWSI. The middle panel shows mid latitude BP with a seasonal deep chlorophyll maximum (PAP). The right panel shows the subtropical oligotrophic variants of the BP with $N_2$ primed and event driven systems in subtropical gyres (NASG/SASG).

Three OBP variants are recognised: a) the Redfield Ratio scenario, with a steady-state stoichiometric balance of C:N:P between exported material and the nutrient supply from the sub-euphotic zone; b) the N-primed prokaryote pump where a proportion of the new organic matter is derived from $N_2$ fixation; and c) the event-driven pump in which a steady-state balance is perturbed physically or biologically by a short term event such as aeolian deposition. We recognise there are sub-variants on the above. For instance, selective subeuphotic zone remineralisation of N/P relative to C can also shift the Redfield OBP situation to that of the N-primed OBP, resulting in enhanced C export. Sub-euphotic biogeochemical processes are covered in Theme 5 which addresses the biogeochemistry of the deep ocean.

While only the Redfield OBP has been studied in detail,

an understanding of the other variants is required particularly since they may be the most efficient means of sequestering atmospheric $CO_2$ (Karl *et al*., 2003). The OBP is now considered susceptible to climate change via mechanisms shown in Figure 1.

### Aim and objectives

Our aim is to carry out a mechanistic evaluation of the OBP in key regions of the Atlantic and assess the susceptibility of OBP processes to climate change. In contrasting biomes, we will determine, through observations, experiments and modelling:

- the role of physical processes for introducing subeuphotic nutrients into the euphotic zone
- the structure and biogeochemistry of plankton communities in the euphotic zone
- the linkage between export from the euphotic zone and plankton community structure.

We will model all elements in an integrated manner and predict the sensitivity of the OBP to climate change scenarios.

### Approach and methodologies

Closely linked with Sustained Observations (SOs) in Theme 10, we will carry out an integrated multidisciplinary research programme in the Atlantic between 60°N and 50°S (Figure 2) in biomes considered vulnerable to change (Sarmiento *et al*., 2004a) and representative of different variants of the OBP (Figure 1). Our prime sites will be in the eutrophic subpolar gyre at OWS India (60°N 20°W; on the extended Ellett line, SO 4), and in the central North Atlantic subtropical gyre (NASG: 24°N 40°W) on the Atlantic Meridional Transect line (SO1) in oligotrophic waters susceptible to Saharan dust inputs. We will also work at an oligotrophic site with lower aeolian inputs in the central South Atlantic subtropical gyre (SASG: 16°S 30°W, also on the AMT line SO 1), and the PAP site (49°N 16°W, SO 2), intermediate in nutrient status between OWS India and NASG. All sites are in the Atlantic, the ocean of most relevance to the UK and, collectively, they give access to the three OBP variants identified earlier (Figure 1). Supplementary background data are available from the long-term observatory at PAP (Theme 5 and SO 2); from the JGOFS time-series at OSW India; and from the RAPID mooring array at the NASG site (joint work with Theme 1).

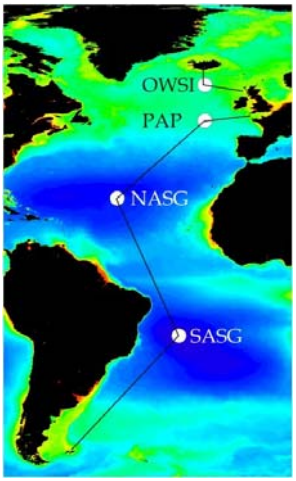


**Figure 2**: Chart showing locations of process studies; OWSI on the Ellett transect and PAP, NASG & SASG on the AMT transect set against a background of SeaWifs chlorophyll (blue/dark is low and green/light is high concentration)

NOC work in Theme 2 will comprise a series of locally intensive process studies and spatially extensive surveys, supplemented by remote sensing and modelling. We will conduct intensive process cruises at OWS India and the NASG site making repeated hydrographic, biological, chemical and export measurements at high spatial resolution in a box using CTD stations and towed instruments to quantify variables and their short term dynamics (Allen *et al*., 2001; Martin & Richards, 2001; Allen *et al*., 2005). In addition, an intensive process cruise at PAP will be undertaken as part of Theme 5. Studies in the SASG will be developed using external funding.

During the programme, we will use Autosub to provide time-resolved 3D fields around the research ship to generate mesoscale spatial context of phytoplankton (*in situ* cytometer and fluorometer), physics (CTD) and chemistry (UV nitrate sensor) fields. This initiative, planned to begin in 2006, will extend our shipboard capability which currently has to balance the requirements for spatial surveying and experimental studies at a central reference station. In parallel, we will use Seasoar to provide complementary data and to estimate mesoscale nutrient fluxes into the euphotic zone. These process studies will give information over a limited part of the seasonal cycle over small regions. Spatially extensive studies made on AMT and Ellett line cruises (Theme 10) will be used together with satellite imagery, to scale up spatially and

temporally from process studies. PELAGRA traps will be used to quantify short term export (Saw *et al.*, 2004) while deep sediment traps (Theme 5) will be used to compare long term particle flux with production estimates from remote sensing, transects and process studies.

Two scales of modelling will be used. At scales of ~1km resolution, the Harvard Ocean Prediction System (HOPS) model will be used in conjunction with the fine-scale surveys to quantify nutrient inputs to the euphotic zone, identify key export related processes and estimate downward export from the euphotic zone. Post-cruise sensitivity experiments will examine the potential for export to be influenced by climate change by imposing scenarios representing potential extreme cases of change, such as increased frequency of storm events, increased heating and stratification of surface waters and increased aeolian deposition. At broader scales, factors controlling nutrient supply, ecosystem structure and export will be studied using the NEMO (Nucleus for European Modelling of the Ocean) model which is a major focus for model development in Theme 9. NEMO will be run globally at ¼º with biogeochemistry, and with a higher resolution (1/12º) nested model for our sites in the North Atlantic. As with the HOPS model, climate sensitivity experiments will be undertaken; e.g. by imposing repeated forcing for particularly windy winters or warm summers.Both approaches will involve the parallel development and incorporation into HOPS and NEMO of ecosystem models including processes of particular interest in the context of changing climate, such as Fe limitation and $N_2$ fixation, and the inclusion of new plankton functional types. The development of this model will be aided by the ecosystem testbed approach proposed in Theme 9.

This research will be delivered by three work-packages, WP 2.5 – 2.7, covering physical processes, plankton communities and export processes. Although described separately below, all will work in an integrated way through multidisciplinary cruises, data analysis and modelling.

## WP 2.5 (NOC) Physical processes and the supply of nutrients to the euphotic zone

### Specific objectives

i) To determine the relative importance of mechanisms effecting nutrient supply to the photic zone by quantifying them in the three major biomes of the North Atlantic.
ii) To establish how representative process studies are for the basin scale and thus define operators to scale up the individual process study results.
iii) To determine the sensitivity to future climate change of the mechanisms sustaining total nutrient supply to the photic zone over the three major biomes of the North Atlantic.

### Rationale

The supply of nutrients to the euphotic zone exerts a fundamental control on the OBP. Physical circulation processes provide many of the biologically available nutrients which fuel new production. Future climate change may perturb the ocean circulation via an increased mean global temperature and changes to prevailing winds. How will future climate change affect export via perturbations to the physical circulation?

Many physical pathways influence nutrient supply: winter overturning (Williams *et al*., 2000); Ekman pumping (Williams & Follows, 1998); small scale turbulent mixing (Lewis *et al*., 1986) and mesoscale ageostrophic circulations (Martin & Richards, 2001; Allen *et al*., 2005), of which eddy-pumping (Martin & Pondaven, 2003; Williams & Follows, 2003) is but one example (Allen, 2005). Increased stratification (Sarmiento *et al*., 2004a) will change patterns of winter overturning and dampen small-scale mixing. Shifts in wind patterns will perturb Ekman pumping. Changes in gradients of ocean heating and wind-forcing will alter the distribution of potential energy released through baroclinic instability of eddies and fronts (Stammer, 1997). The combined effect of change on total nutrient supply will therefore be complex. Can we quantifiably support the predictions of Sarmiento *et al.* (2004a)? Such physically-mediated changes, coupled to changes in aeolian dust deposition, may profoundly alter upper ocean plankton communities, biogeochemical cycling and carbon export.

## Approaches and methodologies

We will study the mechanisms sustaining total nutrient supply to the photic zone by combining data from process studies, SOs and forecast modelling. Through a focus on localised regions, we will extend advances already made by combining operational modelling and high resolution observations (Popova *et al*., 2002; Allen *et al*., 2005). This research confirmed the scale dependent modelling studies of Levy *et al*., (2001), showing that vertical circulations associated with interacting eddies and fronts can double the nutrient flux associated with winter overturning within ~22 days (Allen *et al*., 2005), with a corresponding potential for enhanced export. We will quantify the relative contributions of the different physical pathways identified above to the total nutrient flux, initially at OWS India, NASG and PAP. Such a budget has only previously been attempted at BATS (McGillicuddy *et al.,* 1998; Siegel *et al.,* 1999). By choosing locations representative of large biomes (subpolar, seasonally-stratified subtropical and permanently stratified subtropical; Sarmiento *et al*., 2004a), the results of fine-scale surveys and time-series will be integrated with modelling work and larger scale observations from AMT, satellites and seasonal climatologies. The overall outcome will be a basin-scale picture, that quantifies the sensitivity of the component and total nutrient pathways to changes in warming and wind fields.

### *Process studies*

During each cruise, we will estimate the vertical transport of nutrients associated with mesoscale processes by solving the omega equation (Allen *et al*., 2005, Garabato *et al*., 2002). Differences between the surveys will be used to estimate rates of change in biogeochemical properties. Our strategy will, for the first time, give a sufficient number of rapidly repeated surveys to observe vertical transport, thereby offering a major advance in observational oceanography. For this purpose, the Seasoar system will be upgraded with a laser OPC (LOPC), second generation FRR fluorometer (SAtlantic/Chelsea) and UV nitrate sensor. We will quantify the small-scale vertical mixing flux using nutrient profiles and observations of "diffusive" mixing using ArgoDOT (Smeed *et al.,* 2005), while the STEAP profiler being developed at NOC will offer SOFI opportunities. Post cruise, we will quantify the sensitivity of these two nutrient pathways to projected changes in physical forcing, which may affect the circulation. The HOPS model will be used to provide a detailed analysis of the physics and nutrient pathways at each of the process studies. An inert model tracer introduced below the pycnocline will be used to quantify vertical nutrient flux. Sensitivity tests will then be run in which stratification, wind-forcing and surface heating are altered.

### *Analysis of long-term observations*

Measurements made on time series occupations will be expanded to match those made on process study cruises. On the extended Ellett line (SO 4, Theme 10), physical and nutrient observations, will be complemented by biogeochemical (WP 2.6) and turbulence measurements. Argo floats will be deployed to measure the depth of winter mixing. On AMT, biogeochemical measurements made under SO 1 will be complemented by improved physical measurements to closely match those of process cruises, providing information on a broader scale of the abundance, strength and structure of mesoscale features. Novel techniques will be used to improve horizontal resolution of the coarse CTD spacing; using vessel-mounted ADCP, boundaries between upper ocean water masses, edges of eddies and unstable fronts will be determined from the position of strong current gradients and compared with near real-time satellite SST, altimetry and colour data. Lowered ADCP profiles will be used in conjunction with CTD profiles to quantify variability in geostrophic flow.

### *Large-scale synthesis*

The purpose of this activity is twofold. First we will quantify the magnitude and sensitivity of nutrient fluxes associated with winter overturning and Ekman pumping. For overturning, this will be achieved using time-series (PAP, SO2), Argo floats and mooring data together with previous studies (Williams *et al*., 2000) and basin-scale simulations (NEMO both at ¼º and with a smaller scale nested component at 1/12º in the North Atlantic). For Ekman pumping, gyre-scale gradients in nutrients will be combined with basin scale models to infer horizontal and vertical Ekman fluxes. Results will be compared to previous studies (Williams & Follows, 1998). For both pathways,

sensitivity to change will be quantified by re-running the models with perturbed wind and heat forcing. Second, we will use observations to put the vertical small-scale mixing and mesoscale circulation nutrient pathways into a broader context. For small scale mixing, we will use nutrient and density profiles, together with parameterisations of mixing in terms of stratification and shear, to determine the sensitivity of this flux to changes in stratification over basin scales. For mesoscale circulations, we will use statistics on mesoscale physical variability, to examine how well the surveyed regions represent their biome. We will also use HOPS to determine the sensitivity of this pathway to different levels of mesoscale activity by doing sensitivity runs with modified background density gradients. Together these will allow us to make a first order evaluation of the sensitivity of mesoscale nutrient fluxes on a basin scale to climate change scenarios. In this synthesis, variability in time-series, e.g. from PAP (SO2), will be used in choosing parameters for sensitivity runs to take seasonal variability into account. Finally, we will assess how the relative contributions of the various pathways vary across the North Atlantic (McGillicuddy *et al* 2003) and the sensitivity of their absolute and relative contributions to climate change (Sarmiento *et al* 2004a).

## WP 2.6 (NOC) Plankton communities and biogeochemistry

### Specific objectives

i) To evaluate grazing, light and iron limitation as causes of the residual summer nitrate pool in the high latitude North Atlantic
ii) To investigate the difference in P dynamics and export between the NASG and SASG in particular the influence of advection and dust iron controls
iii) To provide estimates of spatial variability up to a biome scale of planktonic populations and biogeochemical processes related to the above hypotheses
iv) To examine the above hypotheses using ecosystem, HOPS and NEMO models.

### Rationale

The impact of climatic forcing on plankton in different regions is complex with poorly understood consequences for the OBP. However, there is growing evidence that both high and low latitude ecosystems are particularly susceptible to change (Sarmiento *et al* 2004a). In the subpolar Atlantic, the biogeochemical paradigm is one of diatom-dominated spring blooms initiated by $NO_3$ and Si concentrations set by winter overturning (Henson *et al* 2006) which drive carbon export (Sarmiento *et al* 2004a; Allen *et al* 2005). But by late spring and early summer, nutrient limitation and grazing pressure shift phytoplankton community structure towards dinoflagellates and sometimes massive coccolithophore blooms (Holligan *et al* 1993) characterised by calcification rather than silicification processes (Holligan *et al* 1993; Brown *et al* 2003; Moore *et al* 2005). High residual nitrate concentrations and low chlorophyll levels in the Irminger basin in late summer away from coastal margins suggest potential iron control over phytoplankton growth (Sanders *et al* 2005). But it is possible that grazing or light limitation may be responsible for the residual summer nitrate pool. The iron limitation, grazing and light hypotheses will be tested in the high latitude North Atlantic, including the Irminger basin. In addition the factors controlling the transition to calcareous and non-mineralising organisms will be examined as calcite may be important in downwards organic carbon export via the ballast effect (e.g. Klaas & Archer, 2002; see WP 2.7).

Low-latitude oligotrophic subtropical gyres form the world's largest biomes. Covering a third of the Earth's surface, they are dominated by microbial communities that turn over nutrients rapidly in strongly stratified nutrient-poor surface waters. Low nutrient levels make these systems finely balanced with considerable potential for change. In the North Pacific gyre, recent changes have strengthened stratification, favouring $N_2$ fixation. This increased the nitrogen pool, with the system becoming increasingly P limited (Karl *et al* 2001). In the NASG, the potential for P limitation is now thought to be higher than that in the Pacific (Ammerman *et al* 2003).

In the two Atlantic gyres, P concentrations are dramatically different (Figure 3). The supply of nutrients to the mixed layer could be attributed to vertical (WP 2.5) as well as horizontal advection. The latter could be important in establishing the availability of nutrients (Palter *et al*, 2005)

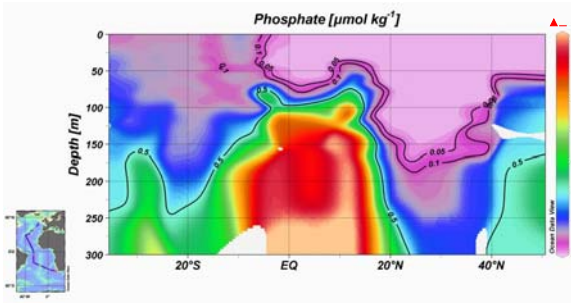


**Figure 3**. Phosphate concentration in the Atlantic ocean on the cruise track (inset) of AMT 17, Nov 2005
(© Plymouth Marine Laboratory)

## Approach and methodologies

We hypothesise that the lower NASG P levels observed are caused by the shallower depth of the deep chlorophyll maximum and enhanced growth of $N_2$ fixers in the NASG gyre promoted by trade wind transported Sahel dust leading to higher levels of carbon export in this region. We will assess the response of the two Atlantic gyre systems, which differ in their properties, to climate change, by comparing their C, N, P and Fe nutrient fluxes and associated biogeo-chemistry including export and biogases, together with an assessment of the contrib.-ution of these biomes to the global OBP.

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### *Process studies*

On process cruises, phytoplankton community structure and biogeochemistry in the euphotic zone will be studied with emphasis on functional groups (diatoms, coccolithophores and picophyto-plankton, including nitrogen fixers) thought to play key roles in the OBP. Complementary approaches of HPLC and flow cytometry with tracer isotope uptake measurements, nutrient limitation experiments and remote sensing will be used. A new HPLC system will be deployed to quantify plant pigments (Llewellyn *et al* 2005) to improve sample throughput capability. Using flow cytometry, bacterioplankton and small protists will be quantified, while FlowCam will be used for larger nanoplankton, microplankton and small mesozooplankton. LOPC backed up with net hauls will be used to quantify mesozooplankton. Particulate calcite, opal, and POM measurements will be made together with the isotopic composition of PON. SAPS will be used for *in situ* pumped sampling (see WP 2.7). Dissolved organic C and N will be measured to estimate the fraction of photosynthetically fixed carbon and nitrogen which accumulates over seasonal timescales (Sanders *et al*, 2005) and may be mixed down and exported. The downward mixing of these phases will be evaluated in collaboration with WP 2.7.

Phytoplankton activity will be quantified using simulated *in situ* incubations using stable and radioisotope tracers including $^{32}$Si, $^{15}$N (for nitrogen fixation, and nitrate and ammonium uptake) and $^{14}$C (for calcification and photosynthesis) (Brown *et al* 2003; Allen *et al* 2005, Painter *et al* 2005; Poulton *et al* 2006). The potential for iron and dust to control nitrogen fixation and planktonic photosynthesis will be assessed using incubation experiments (Mills *et al* 2004) and the current light and nutrient stress of the plankton community evaluated using *in situ* and shipboard FRR fluorometry (Moore *et al* 2005, Holeton *et al* 2005). Bacterioplankton production and grazing loss will be determined (Zubkov *et al* 2000). We will examine the recycling rates of key micronutrients and turnover of labile DOM using tracer bioassay experiments including $^{33}$P and $^{55}$Fe (Zubkov *et al* 2004; Zubkov & Warwick, unpublished AMT and CROZEX).

Flow cytometric sorting (Burkill & Gallienne, 2001) and molecular identification of dominant plankton (Zubkov *et al* 2001) in the euphotic zone will be undertaken. This will focus on cyano-bacteria, the SAR11 group and other prokaryotes (Mary *et al* 2006 a, b) as well as phototrophic and heterotrophic protists (Biegala *et al* 2005). The deep chlorophyll maximum (DCM) flora, including diatoms and coccolithophores, will be analysed and their activity quantified as described above. Algal and microbial mortality by protist grazing will be measured directly (Zubkov *et al* 2000;

Zubkov & Heywood, unpublished AMT data) and indirectly by zooplankton from size class biomass measurements and allometric biomass specific grazing coefficients.

***Long- term wide-field observations***

We will use a subset of the standard suite of measurements described above on SO transects (Theme 10) and use satellite remote sensing to provide a long-term wide-field perspective. We will deploy a suite of in-line instruments capable of characterising the plankton size range from 1µm to 10mm diameter. This suite will produce continuous real-time size-distributed biomass data on organisms classified by functional group. Techniques will be based on established and new flow cytometric protocols for online and high-speed syringe pump counting of phytoplankton, bacteria and protists using new and existing cytometers (Heywood *et al* 2006; Zubkov & Burkill, unpublished AMT data) will be used along with quantification and characterisation using genomic probes (Zubkov *et al* 2001; Mary *et al* 2006a, b) for functional group analyses (Burkill & Gallienne, 2001). Zooplankton will be quantified using FlowCam and Seasoar equipped with OPC. This approach will provide an estimate of spatial variability in microbial populations (Martin *et al* 2005).

Satellite derived ocean colour, sea surface height (radar altimetry) and sea surface temperature (infrared and passive microwave) measurements will be used to integrate process and SO measurements and to scale-up results to biome scale. Satellite derived biological parameters (chlorophyll from ocean colour) together with established production algorithms will allow linkage of the satellite and *in situ* measurements. Algorithms will be tested using our data and protocols refined if necessary before extrapolating to biome scale. Linkages between remote sensing and flow cytometry will be further developed (Zubkov & Quartly, 2003).

Extended Ellett line (SO 4) and AMT transects (SO1) will together be used to study the spatial distribution and abundance of calcifying microorganisms between Iceland and the Falkland Islands, and the environmental controls on their production of calcium carbonate. The leading candidates are: a) water column stability; b) high irradiance; c) low silicate or other nutrient concentrations and the ratios between them; and d) high $CaCO_3$ saturation state (Tyrrell & Merico, 2004).

***Modelling***

Ecosystem modelling will be used to examine the hypothesised differences in iron cycling, phosphorus levels, nitrogen fixation and export between the NASG and SASG sites and to evaluate the potential roles of iron, grazing and other factors in controlling community structure in the North Atlantic subpolar gyre. A new ecosystem model will be developed for this purpose, based on work at BATS (Anderson & Pondaven, 2003) and recent modelling of iron in the Southern Ocean and North Atlantic (Fasham *et al* 2006). Initial development will use 1D models, linking to the test beds formulated in Theme 9. HOPS will be set up and run for NASG, in parallel with the fine scale survey to aid in the design of this survey (Popova *et al* 2002). Controls over community structure at the basin scale and consequences for export (WP 2.7) will be studied using the NEMO model

## WP 2.7 (NOC) Export into the ocean's interior

### Specific objectives

i) To estimate carbon export from the photic zone on process cruises using free drifting traps, deficits of naturally occurring radionuclides, $^{15}N$ assimilation, nutrient depletion calculations and satellite remote sensing
ii) To link the fraction of production exported to biomineral levels, grazing and the size distribution of the plankton using simple parameterisations and models.

### Rationale

We will determine the role of community structure and function in the process of particulate export from the euphotic zone. We will focus particularly on the role that algal biominerals, such as calcium carbonate and opal, may play as ballast agents carrying material into the ocean's interior due to their high density and possible protective action for organic carbon. The relative importance of calcium carbonate and opal is important for deep flux. Klaas & Archer (2002) have commented

"most of the organic carbon rain in the deep sea is carried by calcium carbonate because it is denser than opal and more abundant than terrigeneous material". The processes that underpin this are little known and disputed (Passow, 2004).

Low latitude systems, where most ocean calcification occurs (Sarmiento *et al* 2002) and where diatom productivity appears to be low (Poulton *et al* 2006), may only export from the euphotic zone a small fraction of the carbon they fix (see Fig 1); however, this material may be efficiently transferred to the deep ocean (Francois *et al* 2002). This contrasts with higher latitude systems, in which diatoms may dominate export (e.g. Sanders *et a*l 2005) and where high fractions of fixed material may leave the surface, but with greater losses occurring in the twilight zone (Francois *et al* 2002). To test the hypothesis that export is linked to ecosystem structure and function, we will compare our export measurements with biomineral standing stocks, production rates, grazing and plankton taxonomy (data from WP 2.6). The deeper element will be tested by comparing estimates of export in diverse regions with estimates of transfer through the twilight zone (from Theme 5). Recent studies have suggested that a large fraction of the production-export ratio can be explained by a mechanistic model which considers the size structure of the plankton community and has a simple power law based formulation of grazing (Dunne *et al* 2005). Our focus on biominerals will therefore be complemented by relating export from the euphotic zone to measurements of plankton size structure and grazing, obtained under WP 2.6.

### Approach and methodologies

We have established multiple techniques to estimate the downward flux from the mixed layer and will use them at contrasting sites where surface community structure will vary. A comparison of our export estimates with estimates of the surface production of organic carbon, biominerals, particulate phosphorus and nitrogen and the structure of the planktonic community made under WP 2.6, will allow us to evaluate how the fraction of fixed material which is exported is linked to community structure. These studies will also provide estimates of elemental export to the twilight zone for Theme 5. Consequences of changing climate on export will be investigated using the HOPS and NEMO models, linking to WPs 2.5 and 2.6.

#### *Process studies*

Instantaneous relationships between $^{234}$Th derived export and primary production indicate that production and export are often temporally decoupled from each other (Buesseler, 1998). During process cruises, we will observe the time evolution of both net production and export, and hence develop more accurate parameterisation of the processes that mediate recycling and export from the euphotic zone. Shallow sediment traps are almost always contaminated by zooplankton and suffer from hydrodynamic artefacts. Under BICEP, we have developed a free drifting sediment trap that vastly reduces 'swimmer' contamination and hydrodynamic biases and this will be used at each site to determine downward fluxes of state variables as described above. We will use the $^{234}$Th technique, which we have used to delineate export in diverse provinces along the AMT transect (Thomalla *et al* 2006), to estimate export from the euphotic zone over a timescale of ~30 days. Measurements of $^{15}$N uptake, which we have shown on AMT to yield consistent estimates of carbon export, will be made (e.g. Painter *et al* 2006). Nutrient depletion calculations (Sanders *et al* 2005), which our observations from CROZEX suggest are viable over periods of less than a month in a single area, will also be used to estimate new production from field data.

#### *Long-term wide-field observations*

We will use transect cruise and satellite data to determine the extent to which our selected sites are representative of the Atlantic. We will compare upper ocean community structure, biomineral production and particle characteristics (from WP 2.6) with estimates of net production from nitrate and silicate fields (Sarmiento *et al* 2002, 2004b; Sanders *et al* 2005) and export estimated from $^{234}$Th depletions (Thomalla *et al* 2006). The transect relationships will be compared to those obtained from process studies. Satellite derived processes such as those developed to estimate new production will be compared to the different functional plankton types (Henson *et al* 2003, 2006), and validated against export estimates made via traps. Sediment trap material will be analysed for

biogenic and mineral components including biochemical markers of functional groups, phosphorous concentrations and the isotopic composition of particulate N (Lampitt *et al* 2001; Faul *et al* 2005).

***Modelling***

Building on WPs 2.5 and 2.6, the relationship between ocean physics, plankton community structure and export will be studied using both the HOPS and NEMO models. Sensitivity of predicted export to different parameterisations, particularly those for the influence of ballast on sinking flux, will be investigated. The climate sensitivity experiments carried out using both models will be informative regarding potential changes in the quantity and quality of export in response to changing climate, providing the necessary input into the subsequent study of organic matter transport through the deep water column (Theme 5).

**Summary research plan and deliverables for WP 2.5 – 2.7**

| | |
|---|---|
| 2007 | • Process cruise to OWS India |
| 2007-11 | • Process studies and longterm, wide-field observations (all WPs)<br>• Fieldwork at PAP, via AMT (in 2007, 2008 and 2010) |
| 2008 | • High intensity work on extended Ellett line |
| 2008-12 | • Large scale synthesis (all WPs) |
| 2009 | • Process cruise at PAP site |
| 2010 | • High intensity work on extended Ellett line |
| 2011 | • Process cruise at NASG site |

Our field plan (summarised above) involves process studies in each biome, using data from remote sensing and SO activities (Theme 10) to extend spatial and temporal scales, working with PML on AMT transects (SO1) and SAMS on annual extended Ellett line transects (SO4). Remote sensing and modelling will be carried out through the whole programme.

AMT (SO1) will be used to service the sediment traps deployed in the North and South Atlantic subtropical gyres and to make additional relevant observations. Cruises will be shared with Theme 5 work on the biogeochemistry of the deep ocean, using the same sites/biomes. The Research Unit will deliver a new understanding of the impact of climate sensitive processes on biogeochemistry, plankton community structure, and a climate sensitive evaluation of the OBP using coupled biogeochemical/ physical models. The latter will be suitable for inclusion in basin scale GCMs to allow future predictions of changes in the biological pump.. There will be excellent opportunities for additional collaborations, and for students to be trained in cutting-edge ocean biogeochemistry.

This Research Unit will deliver the following:

- Techniques to use Autosub as a vehicle to support biogeochemical research.
- Quantified processes delivering nutrients to the photic zone in diverse physical regimes.
- Model outputs from HOPS of fine-scale surveys along with experiments on altered forcing.
- Datasets of phytoplankton functional group abundance and their relationship to climatically sensitive variables.
- Nutrient uptake and recycling rates by dominant planktonic functional groups & an assessment of the sensitivity to fluctuations in nutrient concentrations.
- Assessment of the linkage between carbon export and ecosystem structure, particularly size structure, biomineral production and grazing.
- High quality data sets archived with BODC and available to the international community.
- A prediction of the response of the Atlantic Ocean biological carbon pump to climate change.

# Cellular and molecular responses of calcification to rapid global change *Contribution to Theme 2 by the Marine Biological Association*

### Background

MBA will contribute to Theme 2 by investigating the unique attributes of oceanic calcifying phytoplankton and how these key functional groups will respond to global change. The proposed work will lead to a better understanding of species distributions, seasonal succession and global biogeochemical cycling, by providing knowledge of cellular processes that underpin the development of mechanistic models of phytoplankton growth. This research will also provide functional information relevant to NERC programmes such as QUEST, UK SOLAS and CASIX.

### Overall scientific aims

Determining how cellular processes in unicellular organisms mediate biologically-driven carbon and nutrient transformations in the ocean is crucial for modelling the interplay between primary production and nutrient cycling. It is also the basis for understanding how key biogeochemical processes such as calcification will respond or adapt to global change scenarios. In order to achieve the goal of complex, predictive, error-constrained models of population dynamics, assemblage structure and nutrient fluxes, empirically derived models of biogeochemical cycles need to be informed by a full mechanistic understanding of the cellular processes that determine productivity and succession in different phytoplankton groups. Coccolithophores account for ~50% of global marine calcification and provide a major component of the flux of particulate inorganic carbon to the deep ocean. Coccolithophore calcification has been shown to be reduced by elevated atmospheric $CO_2$ in short-term experiments, providing a potential feedback component in the complex regulation of atmospheric $CO_2$ (e.g. Riebesell *et al*., 2000).

The main aims of this Research Unit are to:

- Provide detailed mechanistic understanding of cellular processes mediating calcification in coccolithophores and determine how these are impacted by environmental change with a focus on elevated $CO_2$ and ocean acidification
- Determine how intra- and inter-specific genetic diversity and physiological plasticity in coccolithophores are affected in a rapidly changing environment.

These aims match the strategic goals of the MBA Cell and Molecular Processes programme in addressing mechanisms and responses of marine calcification, coccolithophore diversity and adaptation, to determine how these processes are impacted by rapid global change. The proposed work builds on MBA expertise and capability for phytoplankton cell and molecular physiology (graded $\alpha$5 in 2005 NERC SMA) with extensive collaborative links, including the Leverhulme Trust-funded *Emiliania huxleyi* genome project and the EU Marine Genomics and DIATOMICS projects. This Research Unit will use a number of important novel approaches, including:

- Development of new imaging, cell physiology and molecular approaches not previously applied to phytoplankton.
- Exploitation of Continuous Plankton Recorder (CPR) samples for spatial and temporal mapping of coccolithophore genetic diversity.
- Exploitation of *Emiliania huxleyi* genomics and transcriptomics databases though participation in an on-going international collaborative consortium and annotation team.
- Exploitation of more than 200 *E. huxleyi* isolates held in the Plymouth Algal Culture Collection and development of process-specific molecular probes for calcification.

## WP 2.8 (MBA) Cellular processes that underpin coccolithophore ecophysiology: impact of environmental change.

### Specific objectives

i) Identify coccolithophore membrane transport and nutrient acquisition genes and generate an

annotated 'transportome' for *E. huxleyi*.

ii) Identify components of the signalling machinery, including ion channels that co-ordinate calcification with other cellular processes.

iii) Functionally characterize selected coccolithophore nutrient transporters at the molecular level.

**Rationale**

Production of organic and particulate inorganic carbon in coccolithophores depends on the efficient assimilation of essential nutrients - the first (and least understood) step of which is the transport of nutrients from seawater into the cell. Phytoplankton cells must accumulate inorganic nutrients such as N and P to levels >100 fold higher than the concentrations available in the medium. While the molecular mechanisms of high affinity nutrient uptake in higher plants are well characterised (Buchanan *et al* 2000), they remain largely unknown in phytoplankton. We have identified a number of putative coccolithophore membrane transporters from the available genome sequence information. However, we cannot easily extrapolate function from model "green plant" species to coccolithophorids because of the great phylogenetic distances between them: coccolithophores belong to the kingdom Chromista which is quite separate from both higher plants and animals.

**Approaches and methodologies**

Signalling pathways will be characterised *in situ* using novel membrane biophysical and biochemical approaches coupled with high resolution *in vivo* imaging (e.g. Taylor & Brownlee, 2003; Goddard *et al* 2000). Genome and transcriptome annotation will be used to identify putative transporters, informed by microarray experiments of genes that are differentially expressed in response to culture nutrient limitation experiments. Membership of the *E. huxleyi* Genome Project provides access to the emerging sequence information, microarrays and EST databases. Functional characterization will be carried out in heterologous systems, including *Xenopus* oocytes (facility already established at the MBA), mammalian cell lines, for which incubation facilities are available and, where appropriate, yeast mutants. Gene cloning will be carried out from cDNA libraries by using standard cloning techniques.

## WP 2.9 (MBA) Molecular and cellular determinants of coccolithophore calcification: impact of elevated $CO_2$

**Specific objectives**

i) Characterise inorganic carbon (Ci) and $Ca^{2+}$ entry and trans-cellular transport pathways during calcification in coccolithophores

ii) Use emerging *E. huxleyi* genomics and transcriptomics resources to characterise the calcification machinery at the cellular and molecular level, and determine impacts of elevated $CO_2$ and acidification

iii) Use *E. huxleyi* virus infection as a "non-nutrient" block of calcification

iv) Develop *in situ* molecular probes to assess calcification-related gene expression in the field.

**Rationale**

Coccolithophores and foraminifera together are responsible for the bulk of marine calcification and as such play a fundamental role in global $CO_2$ cycle and carbonate chemistry of the oceans. The metal ratio and stable isotope signatures in marine biogenic calcite are also extensively used to reconstruct past climate over geological time scales (Palmer *et al* 1998; Stoll *et al* 2002). The ability to model the effect of climate change on calcification and provide 'ground truth' of paleoproxies is hampered by our lack of understanding of the specific cellular mechanisms employed to precipitate inorganic carbon in the form of calcite. In coccolithophores this occurs in an intracellular compartment that may be highly buffered from the external environment. Short–term laboratory and mesocosm experiments have shown that increased atmospheric $CO_2$ can lead to reduced coccolithophore calcification (e.g. Riebesell *et al* 2000; Delille *et al* 2005) although with significant inter-species variability (Riebesell *et al* 2000). There is urgent need to understand the molecular mechanisms by which elevated $CO_2$ or decreased pH can affect calcification in coccolithophores.

Viruses exert a fundamental control on algal bloom formation and thus impact many biogeochemical and ecological processes such as species distribution, nutrient cycling, trace gas fluxes (DMS) and system respiration (Fuhrman, 1999). Moreover, viruses play a crucial role in genetic diversity by acting as agents of genetic transfer. Natural marine waters contain $10^6$-$10^9$ virus particles per ml (Bergh *et al*. 1989), mostly bacteriophages (Suttle & Chan, 1993). However, many are also released from infected eukaryotic planktonic microalgae. The recently completed sequence of a giant virus (EhV86) which infects the coccolithophore *E. huxleyi* has revealed that the virus encodes cellular regulatory genes (Wilson *et al* 2005), enabling it to exert control over the host's molecular and cellular machinery in order to replicate. In particular, calcifying *E. huxleyi* strains cease calcification during virus infection (unpublished data) - providing an opportunity to identify calcification-specific genes without the need to manipulate calcification by altering nutrient levels or by comparing genetically different strains.

**Approaches and methodologies**

Trans-cellular transport pathways will be characterised *in situ* with a combination of biophysical, biochemical, electrophysiological and high resolution *in vivo* imaging approaches. Molecular components of the calcification machinery (e.g. ion channels, calcium binding proteins, membrane transporters) will be identified from database annotation, subtractive approaches and microarray analysis of calcifying and non-calcifying cultures. This subset of genes will serve as markers for identifying other calcification-relevant genes identified by microarray analysis of control *E. huxleyi* cultures and those in which calcification has been rapidly terminated by EhV86 infection. We will exploit the EhV86 infection strategy to characterise the molecular pathways that underpin calcification. The impact of elevated $CO_2$ on this calcification machinery will be determined by microarray experiments where total RNA is extracted from chemostat cultures under standard and elevated levels of $CO_2$ at various time points. A comparative analysis of the experimental manipulations will be carried out by grouping and visualising the absolute expressed data (generated by the microarrays) in a hierarchical bi-clustering algorithm. RT-PCR validation will be conducted for genes of interest. The DNA oligo microarrays will represent over 18,000 unigenes from EST libraries from both *E. huxleyi* and EhV86, and are being prepared in collaboration with California State University. We will assess gene expression changes in cruise-collected samples using quantitative PCR and specific calcification-related probes.

## WP 2.10 (MBA) Community structure within coccolithophore blooms: effects of rapid environmental change

**Specific objectives**

i) Determine population genetic structure by analysing the CPR survey silks (since 1938) known from remote sensing and other records to have sampled coccolithophore blooms and determine whether any spatio-temporal changes have occurred in coccolithophore community structure
ii) Characterise the wider phytoplankton communities at the species level, using molecular markers, from archived CPR samples
iii) Validate the CPR molecular data sets by comparison with robust sampling techniques from the same populations
iv) Correlate the species distribution-biodiversity maps with contemporary climate change indicators
v) Determine interspecific physiological plasticity among common North Atlantic coccolithophore species *Coccolithus pelagicus, Gephyrocapsa, Syracosphaera, Calcidiscus* and the A and B morphotypes of *E. huxleyi* grown under varying light, temperature, $CO_2$, pH and UV.

**Rationale**

While a detailed mechanistic understanding of calcite production at the cellular level is crucial to predict changes in calcification under changing physico-chemical properties of the oceans, it is equally important to know to what degree this group of phytoplankton can acclimate (at the physiological level) or adapt (at the genetic level) to a rapidly changing environment. Laboratory

and field work with other microalgal species have shown a lack of specific long-term evolutionary adaptations to elevated $CO_2$; however, it did produce lines that lost the ability to grow well at low $CO_2$ (Collins & Bell, 2004, 2006). *E. huxleyi* calcification and the consequent cellular energetic sink has persisted though natural dramatic global change and currently occurs across a wide range of coastal and open ocean habitats. This suggests that coccolithophore metabolism is highly adaptable. To what degree physiological plasticity or genetic diversity within the species contribute to this is currently unknown. Furthermore, how changing climate ($pCO_2$ and pH) affect the ability to both calcify and sustain high productivity among different species of coccolithophores will have profound implications for the distribution and assemblage structure and their functional roles. For example, the correlation between long time-series data sets such as the SAHFOS continuous plankton recorder (CPR) survey and seawater surface temperatures, has revealed dramatic effects increased seawater temperatures on the phenology at the level of phytoplankton functional groups (Edwards & Richardson 2004, Richardson & Schoeman 2004). We have recently developed a novel technique to reliably extract DNA, amplify and sequence desired phytoplankton PCR products from CPR silks (Ripley *et al*. submitted). This and other state-of-the-art technologies will be used to determine the sensitivity of coccolithophore diversity and biogeography to climate change.

**Approaches and methodologies**

A newly discovered genotypic marker (coccolith morphology motif, CMM) that separates the different *E. huxleyi* strains and morphotypes (Schroeder *et al* 2005) will be used to screen firstly the large *E. huxleyi* culture collection (>200 isolates) held within the Plymouth Culture Collection for species genetic diversity and secondly to "fingerprint" the various natural *E. huxleyi* blooms sampled by the CPR survey. We will utilise additional molecular probes representing a range of taxa (Nejstnaard *et al* 2003; Zhu *et al* 2005) to analyse phytoplankton species diversity. Validation of the CPR molecular data sets will be achieved by performing additional field trials where species diversity profiles as revealed by the CPR can be compared to other robust phytoplankton sampling techniques, (i.e. stringent filtration). In addition, the DISCO (Burkill *et al* 2002) CMM molecular data set revealed a dynamic *E. huxleyi* community diversity (unpublished data) and thus will serve as an excellent data set to validate the CPR survey since CPR samples were also taken in that region at the time of that study (A Walne, SAHFOS; pers. comm.). To determine physiological adaptation, long-term cultures will be grown under varying light, temperature, $CO_2$, pH and UV for measurement of growth rates (Collins & Bell, 2004), photosynthesis and calcification.

**Summary of research plan and deliverables for WP 2.8 – 2.10**

| | |
|---|---|
| 2007-08 | • *E huxleyi* transportome; microarray development and validation |
| 2007-10 | • *E huxleyi* genetic diversity screen; identification and functional characterisation of *E huxleyi* transport/ calcification genes; |
| 2008-12 | • *E huxleyi* nutrient transporters; Ca and Ci uptake analysis; mechanism of coccolithophore calcification |
| 2009-12 | • Impacts of $CO_2$ on gene expression; development of *in situ* molecular calcification probes, CPR screening, physiological diversity studies |

Main deliverables:

- Functional characterisation of membrane transporters driving nutrient uptake in coccolithophores.
- Identification of calcification-relevant genes
- Experimentally verified cellular models of calcification mechanisms and regulation in coccolithophores
- Analysis of the cellular and molecular mechanisms by which elevated $CO_2$ and ocean acidification affect calcification.
- Assessment of the impact environmental change has on the community structure of phytoplankton in general and coccolithophores in particular
- Validation of CPR data for analysis of past phytoplankton assemblages

- Provide mechanistic information for the development of better-constrained models of marine biogeochemical cycles.
- Develop novel molecular, cellular and analytic tools for laboratory and field studies.

# Theme 2 Synthesis and concluding material

### Oceans 2025 synergies and wider links

The three Centres involved in Theme 2 will provide complementary contributions; they will also collaborate in many areas. Dedicated cruises are planned by both PML and NOC, but with the opportunity for scientists from the other Centre to participate. In addition, both PML and NOC will utilise experimental opportunities arising from AMT transect cruises (SO1) to sample both the North and South Atlantic gyres. AMT involves a series of standard measurements but also provides a convenient platform for opportunistic rate measurements. PML and NOC will work together on observational and experimental studies, particularly in the oligotrophic gyres, on natural assemblages and key biogeochemical processes. The overall aim is to maximise cost-effectiveness and added value by increasing synergy between the Centres.

Modelling will also integrate and enhance the measurements made at sea and in the laboratory. Data generated in Theme 2 will be crucial for model development in Theme 9; such models will then enable the results obtained in Theme 2 to be applied to a global context. Linkages with other Themes and existing collaboration with UK and international research groups are summarised in Tables 1 and 2.

**Table 1:** Main links between Theme 2 and other parts of Oceans 2025

| | |
|---|---|
| Theme 1 | Inputs of Ellett line and 26°N physics to aid understanding of local biological and solubility pumps. Links to biogeochemical and ecosystem studies in the Arctic Ocean |
| Theme 3 | Biogeochemical cycles in sediments; effects of sediment resuspension: comparison of surface layer biogeochemistry in shelf seas and its topographic control; acidification effects on benthic species. |
| Theme 4 | Biodiversity of natural assemblages of marine microbes and how biological assemblages change in response to environmental |
| Theme 5 | Surface layer production and export into the twilight zone in contrasting biomes. Reflux of nutrients in the twilight zone to fuel nutrient inputs to surface layer |
| Theme 6 | Hindcast and forecast modelling will place biogeochemical studies in the coastal zone into a wider temporal and geographic context to understand inter-annual variability and long term. |
| Theme 9 | Coupled biological/physical models provide the environmental background (temperature, salinity, biota, etc); ecosystem model development to represent complexity of plankton functional type carbon, nutrient and biogenic gas; development, validation of coupled atmosphere-ocean models – forecast capability. |
| Theme 10 | SO 1: Access to waters of contrasting status (nutrients, communities, export) in Atlantic basin including assessment of long-term observations of export in oligotrophic gyres.<br>SO2: long-term observations on biological pump at PAP site<br>SO4: long-term observations on biological pump at high latitude |
| BODC (NF1) | Data for archive and access to archived data |

**Table 2.** Main existing science collaborations between Theme 2 and other research groups (UK and international) not part of Oceans 2025.

**UK**

| | |
|---|---|
| CASIX | Modelling of air-sea gas exchange processes, development of air-sea flux fields via remote sensing |
| Univ of Dundee | Ocean acidification and algal physiology |
| Univ of East Anglia | Trace gas cycling, atmospheric chemistry, deliberate tracer experiments, air-sea gas exchange processes, marine carbon, oxygen and sulphur cycles, aerosols, microbial nitrogen cycling |
| Univ of Essex | Phytoplankton photophysiology and anti-oxidant mechanisms, iron stress and biogeochemistry in plankton |

| | |
|---|---|
| Univ of Newcastle | Air-sea gas exchange processes, photochemistry, nitrogen fixation |
| Univ of Plymouth | Analytical chemistry (iron and hydrogen peroxide) |
| Univ of Swansea | Virus shunt, organic nutrient cycling, microbial loop dynamics, modelling |
| Univ of Wales Bangor | Turbulence |
| Univ of Warwick | Molecular techniques in marine biogeochemical cycles, and picoplankton |
| University of York | Atmospheric chemistry, sources/sinks of trace gases |

**International**

| | |
|---|---|
| AWI Bremerhaven, Germany | Genomics of phytoplankton/virus interactions, nutrient cycling |
| BSRI Rostock | Microbial ecology of bacterioplankton and protists |
| CSIC, Spain | Microbial processes and trace gas cycling, physics of upwelling |
| Laboratoire d'Océan-ographie Biologique | Nitrogen cycling, dissolved organic nutrients , plankton community production and respiration |
| Lamont Doherty Earth Observatory, USA | Gas exchange processes |
| Leibniz-Inst for Mar Sci | Acidification experiments, iron enrichment experiments |
| MPI Bremen | Molecucular identification of microorganisms |
| MPI Chemie, Germany | Trace gases, gas exchange processes |
| NIOO, Netherlands | Microbial functional biodiversity |
| NIOZ , Netherlands | Near-surface processes, iron enrichment experiments |
| NIWA, New Zealand | Nutrient enrichment experiments, trace gas cycling, nitrogen fixation |
| Univ of Bergen. Norway | Acidification, marine carbon cycle, viral shunt |
| Univ of Bremen, Germany | Gas exchange processes |
| Univ of Miami, USA | Gas exchange processes |
| Princeton Univ, USA | Marine nitrogen and oxygen cycles |
| Univ of Vigo, Spain | Plankton community production and respiration |
| WHOI, USA | Biological pump activities in the N Atlantic |
| Univ of Boston, USA | Modelling of baroclinic instabilities |
| Univ of Brest, France | Nitrification and the F-ratio |
| Univ of Paris | Photographic analysis of particles size distribution for export |

**Theme-wide stakeholder relevance and Knowledge Transfer activities**

Stakeholder relevance and Knowledge Transfer are integral to the Oceans 2025 programme. All marine Centres have obtained and will continue to obtain private sector and government funding for applied research to meet specific end-user needs. Such commissioned research is not presented in this application, but the ability of the marine Centres to attract commissioned research is a direct consequence of previous research that was supported by NERC strategic funding. Oceans 2025 will provide the underpinning capabilities, expertise and facilities that will ensure that the future national needs of the UK can be met. In preparing the Oceans 2025 proposal, major stakeholders were consulted and many of the components have involved discussions with research users. To take that process forward, a Stakeholder Consultation Group will be established for Theme 2 (and other Themes) to meet throughout the duration of the project. The aim will be to ensure effective communication between scientists and research users.

Theme 2 focuses on biogeochemical cycles in the ocean and the way in which marine microbes can influence the atmosphere, by air-sea exchange, and the deep ocean, by sinking of organic matter. These processes are crucial to understanding of the role of the ocean in the Earth system. At a time of rapid climate change, it is essential that global models are parameterised by values obtained by the best techniques. It is also important that the next generation of models incorporate new understanding that emerges from experiments at sea and in the laboratory.

PML, NOC and MBA all have a strong record of transferring knowledge from strategic research to policy issues and to environmental management. This is achieved through good working relation-

ships with government departments and agencies, private sector research users, international bodies and other stakeholders, both through commissioned research and by the provision of advice.

**Table 3.** Examples of policy/application issues and stakeholders in relation to Theme 2 science

| Policy/application issues | Main stakeholders with interests | Relevant Theme 2 science |
|---|---|---|
| The influence of the oceans on the global biogeochemical cycles | IPCC, IMBER, SOLAS, IGBP, Defra, Met Office | C,N and P cycles |
| The influence of the oceans on the global atmosphere | Hadley Centre, NCOF, QUEST UK SOLAS and CASIX | Flux of elements across the air-sea interface |
| Sequestration of atmospheric anthropogenic carbon to the deep ocean | IPCC, IMBER, SOLAS, IGBP, QUEST, MarQuest | Flux of elements across the pycnocline |
| Ocean acidification due to anthropogenic $CO_2$ | Defra | pH effects on microbial activity in the surface ocean |
| Increasing frequency of storms on productivity | Defra, Met Office, NCOF, IMBER, IPCC, IGBP, SCOR | Nutrient supply and stratification effects on phytoplankton productivity |
| Paleo-proxies of ocean temperature | IPCC, Hadley Centre, IMBER, IGBP. | Cellular mechanisms underlying biological fractionation of stable isotopes and metal ions. |

The research described in this proposal does not duplicate work separately funded by NERC directed programmes (e.g. UK SOLAS, Post-Genomics & Proteomics and QUEST) and other NERC funding modes. For example, UK SOLAS has not itself funded any field-based research on long lived greenhouse gases such as carbon dioxide, nitrous oxide and methane, nor on the role of the shelf seas in the air-sea exchange of reactive gases, nor on the impacts of acidification on biogeochemical cycles and biogenic gas cycling.

**Strategic Ocean Funding Initiative (SOFI)**

Up to 10% of the research funding for Oceans 2025 will be made available to UK universities and other academic institutions eligible to receive NERC support. Such funding will be awarded for research that is complementary to the Oceans 2025 science Themes, in defined topic areas in a series of funding calls (first call to be announced in 2007). For Theme 2, the following SOFI opportunities have been identified:

- Production/respiration comparisons would be enhanced by $O_2$ isotope measurements
- Determination of air-sea OVOC fluxes via direct measurements in the atmosphere would add value to those that we will calculate from air and water concentration differences.
- Measurements of changes in metal (e.g. Fe, Zn) concentrations and speciation during incubation experiments
- Study of the small-scale turbulent flux of nutrients
- Inorganic carbon, iron and coccolithophores
- Study of gene expression profiles in chemostat culture and microarray analysis.

**Summary of Theme-wide outcomes**

- Develop a predictive capability for the impact of a high $CO_2$ world on marine biogeochemical cycles.
- Provide quantitative information for the development of better models of marine biogeochemical cycles, including an assessment of major controls on the ratio of photosynthesis and respiration
- Evaluate the impact of climate change on ocean feedbacks to the atmosphere.
- Quantify biogas production, cycling and air-sea fluxes.
- Quantify nutrient supply to the euphotic zone in diverse physical regimes, including the incorporation of nitrogen fixation and nitrification rates into new production estimates.

- Assess the linkage between carbon export and ecosystem structure, particularly for biomineral fluxes.
- Evaluation of the role of viral shunt in biogeochemical cycles.
- Analyse the cellular and molecular mechanisms by which elevated $CO_2$ and ocean acidification affect calcification.
- Investigate how phytoplankton response to stress with the objective of predicting responses to climate change.

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## Acronyms

| | |
|---|---|
| ADCP | Acoustic Doppler Current Profiler |
| AMT | Atlantic Meridional Transect |
| ARGO | A temperature/salinity profiling float |
| ArgoDOT | A turbulence profiling float |
| ASLO | American Society for Limnology and Oceanography |
| Autosub | Autonomous submarine vehicle |
| BATS | Bermuda Atlantic Time Series |
| BODC | British Oceanographic Data Centre |
| CACGP | Commission for Atmospheric Chemistry & Global Pollution |
| CASIX | Centre for Air-Sea Interaction and Fluxes |
| CPR | continuous plankton survey |
| CROZEX | Crozet natural iron bloom and export Experiment |
| CTD | Conductivity, Temperature, Depth |
| DCM | Deep Chlorophyll Maximum |
| Defra | Department of Environment, Fisheries & Rural Affairs |
| DOC | Dissolved organic carbon |
| DON | Dissolved organic nitrogen |
| DMS | dimethylsulphide |
| DMSP | dimethylsulphoniopropionate |
| EGU | European Geophysical Union |
| FRR | Fast repetition rate |
| GCM | General circulation model |
| HEI | Higher Education Institute |
| HOPS | Harvard Ocean Prediction system |
| HPLC | High Performance liquid Chromatography |
| IGBP | International Geosphere Biosphere Programme |
| IMBER | Integrated Marine Biogeochemistry Ecosystem Research |
| IPCC | International Panel on Climate Change |
| JGOFS | Joint Global Ocean Flux Study |
| NASG | North Atlantic Subtropical Gyre |
| NCOF | National Centre for Ocean Forecasting |
| NEMO | Nucleus for European Modelling of the Ocean |
| OBP | Ocean carbon biological pump |
| OPC | Optical Plankton counter |
| OVC | oxygenated volatile organic compounds |
| OWS | Ocean Weather Ship |
| PAP | Porcupine Abyssal Plain |
| PON | Particulate Organic Nitrogen |
| QUEST | Quantifying and Understanding Earth Systems |
| SAHFOS | Sir Alister Hardy Foundation for Ocean Science |
| SASG | South Atlantic subtropical gyre |
| SCOR | Scientific Commission on Ocean Research |
| SO | sustained observation |
| SOFI | Strategic Ocean Funding Initiative |
| SOLAS | Surface Ocean Lower Atmosphere Study |
| SST | Sea Surface Temperature, |
| STEAP | Southampton Turbulence and Environmental Autonomous Profiler |
| WCO | Western Channel Observatory |