Effects on the marine environment of ocean acidification resulting from elevated levels of CO$_2$ in the atmosphere
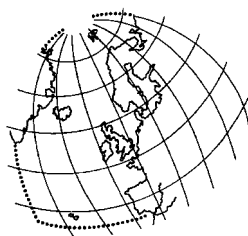
OSPAR Commission
2006

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention") was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.

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Summary

Increasing levels of CO_2 in the atmosphere leads to CO_2 uptake across the air-sea interface and increased carbon concentrations in the ocean. This increases the acidity of the seawater, expressed by a reduced pH. Surface waters of the world oceans have already experienced a pH reduction of about 0,1 pH units. Further reductions of the order of 0,2-0,3 by 2100 are expected and even larger reductions may occur thereafter depending on future emission scenarios. The acidification occurs first in the surface mixed layer which is typically 50 - 200m deep, and with some delay to deeper waters. In regions with efficient ventilation to great depths, such as in the Greenland Sea, waters down to several thousand meters depth may experience acidification rates in this century approaching those of near surface water.

Changes in ocean carbon chemistry due to elevated atmospheric CO_2 are not restricted to increased acidity, i.e. reduced pH. An increased concentration of dissolved CO_2 in seawater also implies reduced concentration of carbonate ions. This has consequences for the carbonate saturation state of the seawater and implies that it is becoming gradually more difficult for marine organisms to build carbonate shells. Corals including those living in cold water coral reefs in the OSPAR maritime area, and some pelagic organisms, including potential key species of phytoplankton and zooplankton, are likely to be significantly negatively affected by the ongoing acidification.

Present changes in ocean carbon chemistry are rapid, at least 100 times more rapid than any experienced over the past 100 000 years. Individual species which may be especially vulnerable have little possibility to adapt, but some species which may exist in different forms e.g. with and without carbonate shells may shift towards dominance of the latter. Ecosystems are likely to change but in yet unpredictable ways. Subpolar marine ecosystems such as those within the OSPAR maritime area are characterized by long generation times and few key species. Chemical properties of the relatively cold water implies a more rapidly reducing carbonate saturation state than at lower latitudes.

It can be concluded with certainty that calcifying organisms will be negatively affected in the present century. However, detailed knowledge about possible other responses in different kinds of organisms to the ongoing changes is very limited. Few experiments have been made. There is basic mechanistic understanding of some physiological processes but no overall assessment of effects and poor baseline information in particular for polar and subpolar seas.

1.   Introduction

Scientific knowledge about effects of elevated CO_2 in the ocean has a short history. Only very recently has the topic and the potential seriousness of direct consequences of anthropogenic CO_2 emissions on marine life through changes in the chemical state of seawater come to the full attention of scientists and policymakers worldwide. This means that the knowledge available is limited. The findings in the scientific literature have in many cases had very short time to mature and come under scrutiny, and the state of knowledge is changing rapidly.

Available evidence comes from several sources. There have been some basic research activities notably within marine animal physiology. The total efforts have been limited with few active research groups, but the published understanding of mechanisms can be considered trustworthy. There have also been some important experiments exposing phytoplankton communities and different calcifiers to realistic future CO_2 levels and demonstrating clear effects. In many cases, however, the knowledge comes from experiments with either relatively rapid or relatively large amplitude environmental perturbations compared to those which are expected as a consequence of invasion of anthropogenic CO_2 from the atmosphere.

The lack of marine experimental data is in stark contrast to the situation for terrestrial systems, where a series of Free Air CO_2 Enrichment (FACE) experiments have been performed in many locations across the globe; a recent report (Ainsworth & Long, 2005) mentioned 120 peer review

papers arising from 12 large scale FACE experiments in the past 15 years. In the marine realm, concern about rising levels of atmospheric CO_2 has primarily dealt with impacts of increasing ocean temperature and sea level, changing ocean currents, mixing and ventilation. But e.g. Hallock (2005) states that the most serious consequence of increasing atmospheric CO_2 concentrations for coral reefs is the one most commonly overlooked, i.e., alteration of ocean chemistry.

Unintentional leakage from subseabed disposal could give local change in ocean carbon chemistry with much larger local amplitude than that arising from invasion from the atmosphere. During the past 10 years there have been some research efforts devoted to the effects of direct ocean storage of CO_2 in the deep sea. Expected local effects may include acute mortality, see the Ocean Chapter of the recent IPCC Special Report on Carbon Dioxide Capture and Storage (Caldeira et al. 2005). In the case of leakage through the seabed, additional effects not addressed in the IPCC report could arise due to the difference between marine biota and environment in relatively shallow water above potential geological storage sites (of order 500m water depth) compared to those at the typical depths considered for ocean storage (3000m water depth). In case of leakage, and in contrast to the case of invasion from the atmosphere, monitoring in the ocean, similar to that envisioned for direct ocean storage schemes (Caldeira et al., 2005) could possibly be used to determine the location of the CO_2 source. To the best of our knowledge, monitoring of the effects on the marine environment of CO_2 from the atmosphere, has never been considered in detail. Effects on the marine environment of CO_2 leakage from seabed storage is not considered further in this report.

Emitted CO_2 spreads rapidly in the atmosphere and contributes to a pressure driving CO_2 into the ocean almost everywhere. The OSPAR maritime area is affected not only by air-sea exchange in the region but also by anthropogenic CO_2 taken up further south and carried by ocean currents into the area from lower latitudes (Lundberg & Haugan, 1996). This illustrates the global character of the ocean acidification problem.

According to the OSPAR convention the contracting parties shall take all possible steps to prevent and eliminate pollution in the area covered by the convention. Pollution here means the introduction by man, directly or indirectly, of substances or energy into the maritime area which results, or is likely to result, in hazards to human health, harm to living resources and marine ecosystems, damage to amenities or interference with other legitimate uses of the sea. It is not within the mandate of the working group to address possible implications of our findings for OSPAR or contracting parties. However, it should be noted that if it is concluded that ocean acidification e.g. leads to harm to marine ecosystems, our scientific understanding of the global carbon cycle suggests that implications ("all possible steps") should involve efforts to limit global CO_2 emissions. The effects on the OSPAR area of CO_2 emissions from elsewhere in the world will be identical to those arising from emissions in bordering countries or from ships or structures within the area.

2. Recent development of relevant assessments and research reports

The scientific literature contains references dating at least 10 years back pointing to possibly severe impacts and underlining the global scale and unprecedented rate of change in the marine environment due to global CO_2 emissions to the atmosphere. However, efforts to create global awareness and even to outline a work programme to the European Commission (Lie, 1998) met with limited response during the 1990s. The OSPAR Quality Status Report from 2000 elaborates on other issues including climate change and variability but does not mention direct CO_2 effects. Impact assessments from the Intergovernmental Panel on Climate Change (IPCC) have so far not described ocean acidification. Climate change research programmes generally seem to have defined direct chemical effects of CO_2 as out of scope. The recent Arctic Climate Impact Assessment (ACIA) does not address acidification.

Despite limited funding, some researchers were able to perform very important work and the accumulated evidence grew, if slowly, around the turn of the century. Some of the available funding came from programs directed at investigating environmental effects of intentional direct

ocean storage of CO$_2$ (Shirayama et al., 2004), but nevertheless provided background knowledge relevant also for atmospheric CO$_2$ effects. Turley et al. (2004) reviewed possible impacts after gradual or catastrophic release from storage. The IPCC Special Report on Carbon Dioxide Capture and Storage from December 2005 in its chapter on ocean storage (Caldeira et al., 2005) includes an up to date general discussion of biological consequences of elevated CO$_2$ in seawater. The focus of that report however is on consequences of intentional direct ocean storage, not atmospheric CO$_2$.

The recent report from the UNEP World Conservation Monitoring Centre on cold water coral reefs (Freiwald et al., 2004) mentions atmospheric CO$_2$ as a potential upcoming threat without going into details. A brief overview report of the general issue of ocean acidification (Haugan, 2004) was presented to OSPAR in early 2005. While it was not the result of another broad assessment, it contributed to the background for setting up the present working group.

Major events in 2004 and 2005 that created increased attention were the May 2004 IOC/SCOR Symposium and the June 2005 release of a Royal Society policy document. The report from a workshop in the US in April 2005 is likely to also become important, particularly for attention in North America and generally in scientific circles, once released in early 2006. In subsequent subsections we briefly describe these three events followed by two upcoming events in 2006. We note that of course it is the individual peer review papers which form the basis for any scientific assessment. Papers in high profile journals like Science and Nature (Riebesell et al., 2000, Caldeira et al., 2003, Feely et al., 2004, Sabine et al., 2004, Orr et al., 2005b) have stimulated much discussion and attention.

2.1   IOC/SCOR Symposium May 2004

Member states of the Intergovernmental Oceanographic Commission (IOC) of UNESCO expressed concerns over potential environmental consequences of using the deep ocean for intentional storage of CO$_2$. In order to be better informed on these issues, IOC contacted the independent international Scientific Committee of Oceanic Research (SCOR) of the International Council of Scientific Unions (ICSU) to co-host a scientific symposium on ocean carbon sequestration science. In addition, a web site with a watching brief on ocean carbon sequestration (http://ioc.unesco.org/iocweb/co2panel/Sequestration.htm) was set up to provide an overview of the current scientific and legal issues of ocean sequestration of CO$_2$ for the Member States of the Intergovernmental Oceanographic Commission, as well as other policymakers and the general public.

The scientific program committee appointed by SCOR and IOC suggested widening the scope of the scientific symposium to also include effects of atmospheric CO$_2$. This was approved by the sponsoring organizations and in May 2004 a symposium on The Ocean in a High CO$_2$ World (http://ioc.unesco.org/iocweb/co2panel/HighOceanCO2.htm) was held in Paris. A research priorities report is available on the web site and in addition two reports were published in EOS and The Oceanography Magazine, respectively (Cicerone et al., 2004a,b). Key scientific papers from the symposium were published in a special issue of Journal of Geophysical Research (Orr et al., 2005a).

2.2   Royal Society report June 2005

The Royal Society in the UK subsequently appointed an expert working group and solicited input from the scientific community to the production of a high profile policy document on ocean acidification due to increasing atmospheric carbon dioxide (Royal Society, 2005, also available on www.royalsoc.ac.uk). It provided an updated account of the science combined with specific policy recommendations such as the need to limit the cumulative CO$_2$ emissions to the atmosphere by 2100 to 900 GtC to avoid irreversible damage arising from ocean acidification. Scientific findings from this study are reflected in more detail in later sections.

2.3   US Workshop on impacts on coral reefs and other marine calcifiers

In April 2005 a Workshop on the Impacts of Increasing Atmospheric CO_2 on Coral Reefs and Other Marine Calcifiers was held in Petersburg, Florida, USA, sponsored by NOAA, NSF and USGS (http://www.isse.ucar.edu/florida/index.html). The full report is not yet available, but the organizers (Tedesco, Feely, Sabine and Cosca) have made available a popular summary report on http://www.oar.noaa.gov/spotlite/archive/spot_gcc.html. The following were some of the major conclusions of the workshop:

1.   Ocean acidification is a predictable consequence of increased atmospheric carbon dioxide concentrations from human activities**.** Surface ocean chemistry CO_2 and pH changes resulting from these activities can be predicted with a high degree of confidence.

2.   Ocean acidification means that there would be concern over carbon dioxide emissions independently and apart from any possible effects of carbon dioxide on the climate system**.** Ocean acidification and climate change are both effects of CO_2 emissions to the atmosphere, but they are completely different; ocean acidification depends on the chemistry of carbon dioxide; whereas climate change depends on temperature and freshwater changes resulting from the atmospheric carbon dioxide and other greenhouse gases.

3.   If current trends in carbon dioxide emissions continue, the ocean will acidify to an extent and at rates that have not occurred for tens of millions of years**.** At present, ocean chemistry is changing at least 100 times more rapidly than it has changed in the 100,000 years preceding our industrial era.

4.   Ocean acidification could be expected to have major negative impacts on corals and other marine organisms that build calcium carbonate shells and skeletons**.** When carbon dioxide reacts with seawater it forms carbonic acid, which is corrosive to calcium carbonate shells and skeletons. The impact is likely to be disruptions through large components of the marine food web. The potential for ecological adaptation is unclear at this time; however, both in today's ocean and over geologic time the rate of accumulation of shells and skeletons made from carbonate minerals shows a consistent relationship with ocean chemical conditions indicating that the success of these organisms is largely controlled by carbonate chemistry.

5.   Research is needed to better understand the vulnerabilities, resilience, and adaptability of marine organisms and ecosystems**.** The science of understanding the biological consequences of ocean acidification, and placing these changes in a historical context, is in its infancy; initial information indicates that there is cause for great concern over the threat carbon dioxide poses for the health of our oceans.

While the topic of this workshop was restricted to calcifiers, the statements above resonate well with those that have emerged from other assessments.

2.4   Ongoing development of knowledge

At the biannual Ocean Sciences meeting in Honolulu in February 2006 hosted by the American Geophysical Union (AGU), the American Society of Limnology and Oceanography (ASLO) and The Oceanography Society (TOS), there will be a special session on "Observations of Anthropogenic Climate Change in the Oceans and Their Implications for Society II: Arctic and Ecosystem Responses". The session starts with an invited talk by Orr (with coauthors) entitled "Arctic Ocean Acidification" and includes talks by Langdon on "Possible consequences of increasing atmospheric CO_2 on coral reef ecosystems" and Caldeira on "Carbon Dioxide and Ocean Chemistry Change: What Does the Geologic Record Tell us About the Future?"

At the annual meeting of the European Geosciences Union in April 2006, for the first time there will be a separate session on the topic "Ocean acidification: chemistry, paleo-analogues, response of organisms and ecosystems, and modelling". The aim of the session is to review recent data on the

chemical, biological, and geological consequences of rising atmospheric CO_2 and resulting ocean acidification. Submissions to this session from a broad geographic, thematic and instrumental range are encouraged by the conveners Jean-Pierre Gattuso (France), Joanie Kleypas (USA), Jim Orr (France) and Ulf Riebesell (Germany). Thus it can be stated that ocean acidification is rapidly becoming a mainstream topic in ocean science worldwide. Yet this research is difficult and it will take time and resources to provide more solid and broad knowledge.

We end this section with a quote from Jim Orr et al (abstract to AGU/ASLO/TOS Ocean Sciences 2006): "Decreases in Arctic carbonate ion concentrations are likely to affect many calcifying organisms, including aragonitic cold-water corals and shelled pteropods, calcitic coccolithophores and foraminifera, as well as high-Mg calcite producing coralline red algae and echinoderms. No data are available on the response of Arctic calcifiers to decreased carbonate saturation state, but evidence from lower latitudes suggests that at least some Arctic calcifiers will suffer reduced calcification, potentially affecting their competitiveness and survival. The added pressure of ocean acidification could reduce biodiversity and alter the food-web structure of both planktonic and benthic Arctic ecosystems. Unfortunately, our poor general understanding of Arctic calcifiers, e.g., even their baseline geographical distributions, means that future changes will be hard to detect." This study can be seen as a supplement or extension of the paper published in Nature in 2005 (Orr et al., 2005b) which described severe consequences in the world ocean, particularly the Southern Ocean, but where the Arctic was not included in the model studies or data analyses. Preliminary findings from the new study underline both the poor baseline knowledge and the potentially severe consequences that can be expected also in the high northern latitudes of particular relevance to OSPAR.

In combination, the references already mentioned document a fairly massive, though recent, consensus in the ocean science community that ocean acidification is a potentially critical issue for the future health of the ocean. The remainder of this report contains an overview of the present state of knowledge of relevance to OSPAR. References given above may be consulted for introduction to basic concepts and later references for more in depth information.

3. Changes in the chemical environment

As already mentioned, CO_2 emissions to the atmosphere spread rapidly. There is a north-south gradient in the atmosphere with higher CO_2 levels in the northern hemisphere than in the southern hemisphere due to emission patterns and oceanic and atmospheric transports. There is also a geographically dependent seasonal cycle both in the atmosphere and the ocean related to seasonal biology. And there are interannual variations in the atmospheric CO_2 trend due to phenomena such as El Nino which involves changes in sea surface temperatures in the Equatorial Pacific with implications for weather patterns and biological responses over large areas. However none of these variations can mask the fact that atmospheric CO_2 concentrations are rising in a geographically uniform way all over the globe on decadal and longer time scales due to the global anthropogenic emissions.

CO_2 enters the well mixed ocean surface layer whenever the partial pressure of CO_2 is higher in the overlying air than in water. The equilibration time is dependent on wind and sea state. But generally in the absence of deep mixing or upwelling, an ocean surface mixed layer of less than several hundred meters depth will have a partial pressure of CO_2, denoted pCO_2, which trails that of the atmosphere on time scales longer than a year. Surface exchange fluxes and the geographical distribution of anthropogenic CO_2 stored in the ocean is strongly affected by horizontal ocean currents, vertical exchange processes and the geographical distribution of biological agents which transform carbon back and forth between the organic and inorganic pools.

In the last 20 years efforts to map the distribution of carbon sources and sinks and the distribution of various forms of carbon in the ocean have been increasing. A consistent picture now emerges. The vertically integrated inventory of anthropogenic carbon per unit area in the ocean is clearly highest in the Northern North Atlantic compared to all other major ocean basins (Sabine et al., 2004). This is related to the relatively weak stratification in the area and the character of the mean ocean circulation which converts surface water to deep water in the Nordic Seas, the Labrador Sea

and generally in the subpolar gyre. This allows deep penetration of the surface signature in anthropogenic CO_2. Much of the anthropogenic CO_2 in the northern parts enters the area via the dominating inflowing current system from the south rather than via local air-sea uptake (Lundberg & Haugan, 1996).

In order to understand past changes in ocean carbon cycling and study future scenarios, numerical ocean circulation carbon cycle models are used (Caldeira & Wickett, 2003, 2005, Heinze, 2004, Orr et al., 2005b). These uniformly predict a continued uptake of anthropogenic CO_2 in the oceans in the future. Assuming fossil fuel reserves corresponding to total emissions of 5270 GtC since pre-industrial times and distributing the emissions over time based on observations up to now, IPCC emission scenario IS92a until 2100, and a logistic function thereafter, Caldeira & Wickett (2003) obtained surface pH reduction of more than 0,7 in year 2300, noting that the surface ocean may then become more acidic than during the past 300 million years with the possible exception of rare, extreme events.

As the ocean becomes more acidic due to higher carbon content, its ability to take up CO_2 reduces. While the chemistry of this buffer effect are well understood, the future uptake may also depend on poorly understood possible responses to increased greenhouse effect such as changes in ocean circulation and ice cover, and indeed on possible changes in ocean biology including such changes which are discussed in the present report. However, even if the ocean in the future may take up a slightly smaller fraction of the emissions on annual basis than the present situation, on a 1000 year time scale, 70-90 % of the cumulative emissions are likely to reside in the ocean. Thus we can be confident that the ocean acidification process will not stop in the future. It will increase in amplitude and be with us for centuries.

Simple calculations suffice for estimating the equilibrium carbon system response in surface water to specified atmospheric partial pressure (Haugan & Drange, 1996, Brewer, 1997). These are suitable for global averages. More detailed calculations for the future can be made in numerical models which account for ocean circulation and represent geographical variations in temperatures and chemical state. Orr et al. (2005b) used such models and found that the Southern Ocean was particularly vulnerable to changes in carbonate saturation state with severe implications for calcifiers (see later sections). Bellerby et al. (2005, Fig. 1b below) focussed on an area relevant to OSPAR, and found that the future pH changes are not expected to be uniform. The main regional gradients are associated with the transition between Atlantic and Arctic waters.

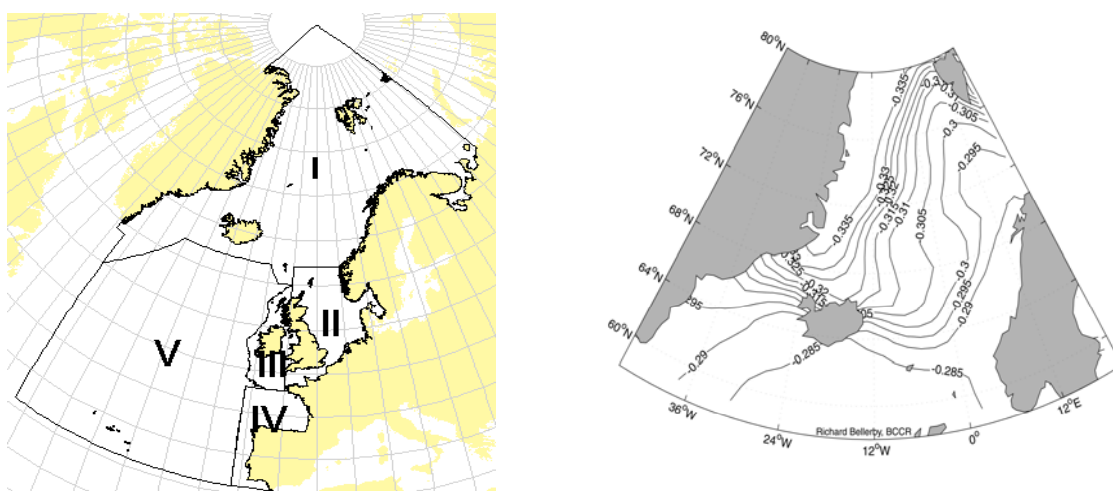*Figure 1a) showing the OSPAR regions and 1b) showing the predicted reduction in surface pH from 1997 to 2067 in a scenario in which atmospheric CO_2 doubles during that time (approximately 1% increase per year). The physical ocean state is taken from coupled climate model run and the surface ocean carbon chemistry from empirical correlations with the physical state. From Bellerby et al. (2005).*

Overviews of ocean carbon chemistry can be found in textbooks such as Zeebe & Wolf-Gladrow (2001). A brief introduction focussed on the issues associated with adding CO_2 to seawater and an overview of scenarios can be found in the IPCC report (Caldeira et al., 2005). Other reports also contain introductory material. A one-page primer on relevant carbon chemistry is included in Haugan (2004). Noting that the pH scale is logarithmic (so that a pH reduction of 1,0 corresponds to a 10-fold increase in the concentration of H^+), the essence for our purposes are contained in the equation given in section 4.1, showing that addition of CO_2 reduces availability of carbonate ion (CO_3^{2-}).

4. CO_2 effects on marine organisms and ecosystems: physiological background and affected processes

Biogeochemical processes that regulate the earth system are determined by the ecosystem functioning and the biodiversity within the ecosystem. Loss or change in biodiversity could therefore have impacts on ecosystem functioning, its biogeochemistry and regulation of the earth system.

So far there are no field observations to prove specific effects of CO_2 in marine ecosystems. Statements on the effect of CO_2 on marine organisms are therefore based on experimental studies in laboratories or, lately, in mesocosms. They are also based on experiments in areas with volcanic CO_2 emission or on few observations after releasing CO_2 into the deep sea. Known effects range from the molecular to the cellular and whole organism level and relate to processes and mechanisms in phytoplankton and some groups of animals. General principles of the effects of CO_2 in all organisms are to be distinguished from those specific and typical for certain groups. This is especially valid in case of animals. Apart from more recent mesocosm studies (Riebesell, 2004) experimental investigations of the effect of CO_2 at ecosystem level are completely missing. Existing mesocosm studies focus on CO_2 effects on primary production and the export of organic material.

In the light of complete lack of field observations, scenarios of CO_2 effects on marine ecosystems developed based on laboratory, mesocosm or even experimental field data will only be reliable when based on a mechanistic cause and effect understanding elaborated in physiological and biochemical studies. In view of the large gaps in knowledge, there is considerable demand for research in this area (Cicerone et al., 2004a,b, Raven et al., 2005, Orr et al., 2005b) to reach predictability. As per latest findings, the effects of CO_2, temperature and oxygen are interacting (Reynaud et al., 2003, Hoegh-Guldberg, 2005, Pörtner et al., 2005d). This requires an integrated analysis of these effects to evaluate the role of CO_2 as well as its interaction with other changing factors more precisely.

Considering the importance of organismic physiology and biochemistry for the understanding of causes and effects, the physiology of the effects of temperature and CO_2 shall be dealt with first. This knowledge includes whether, how and to what extent organisms acclimatize or adapt on evolutionary time scales to changing CO_2 levels. Only with such baseline knowledge, can the sensitivity of higher level processes be understood beyond empirical or modelling studies. Higher level processes comprise changes in biogeographical distribution, in how organisms and their interactions shape biogeochemical processes, in biodiversity and last not least in availability of marine resources for fishery.

When organisms (here marine microorganisms, phytoplankton and water-breathing animals) are surrounded by increased CO_2–concentrations, these conditions are called hypercapnia. Knowledge of the unifying physiological effects of CO_2 on individual organisms is equally important for understanding CO_2 effects on organisms at the ocean surface as on benthic and deep-sea organisms. In surface oceans, photosynthetically active marine organisms, especially phytoplanktonic organisms, are the basis for 99 % of the organic material which enters the seas' food chains. By fixation of about 47 Gt C per year, phytoplankton contributes to nearly half the primary production on earth, macroalgae, sea grass and corals produce additional 1 Gt C per year (Field et al., 1998). Mostly microorganisms (del Giorgio und Williams, 2005), but also zooplankton and larger animals consume the organic carbon, which passes through complex food chains for

the higher trophic levels, animals. A change in ocean chemistry affects all organisms directly, heterotrophic organisms like animals are also indirectly affected through changes in the food chain. Feeding pressure on phytoplankton or other organisms may change due to direct CO_2-effects on plankton grazers.

Some CO_2 effects are elicited through changes in water pH. The effect of lowered pH-values (without simultaneous CO_2 accumulation) was mostly investigated in fresh water organisms and to a lesser extent in marine organisms (Wolff et al., 1988). Effects caused by pH changes comprise changes of productivity in algae (e.g. through changes in the rate of cell division; Hinga, 2002) and in heterotrophic microorganisms (Archaea, bacteria, fungi and protozoans), altered rates of biological calcification and decalcification as well as changes in the rates of metabolism of zooplankton, benthic species and fish. Lowered pH-values in the water impair reproduction of animals in fresh water and in the sea. A low pH in the water leads to smaller egg sizes and delayed hatching (Vinogradov and Komov, 1985). Egg fertilization in mussels is most successful at slightly alkaline pH (Alvarado-Alvarez et al., 1996). Even slight lowering of pH may reduce reproductive success (e.g. Desrosiers et al., 1996). In sturgeons (*Acipenser transmontanus*) sperm mobility is reduced at both low pH as well as at increased pCO$_2$ (Ingermann et al., 2002).

The ability to adapt to increasing CO_2 concentrations on evolutionary time scales is unclear for all groups of organisms. However, the ancestors of extant forms lived under higher CO_2 levels. For marine organisms it is also completely unclear to what extent adaptation to today's values is based on irreversible specialisation on certain windows of CO_2 concentrations. Available tests of experimental evolution (Collins and Bell, 2004) have limited applicability in natural environments.

Results obtained in phytoplankton and macroalgae support an integrative concept for the effects of CO_2 on primary production. This concept is not yet complete, but interprets some phenomena at organismic and ecosystem levels through enzymatic characteristics and cellular transport phenomena and thus shows a way to understanding causes and effects. Such an integrative concept is not yet available for animals, but similar principles may be operative as under the effect of temperature changes (e.g. Pörtner, 2002, Pörtner et al., 2004). Several components and processes have become known in animals, and, as in case of temperature, many CO_2-effects at molecular and cellular levels may finally lead to a lowering of aerobic capacity and scope of animals and thus a restriction of whole animal performance capacity (Pörtner et al., 2005).

4.1   Calcification and calcifying organisms

When CO_2 is dissolved in seawater, there will be a decline in carbonate ion (CO_3^{2-}) concentrations as they react with increased concentrations of anthropogenic CO_2:

$$CO_2 + CO_3^{2-} + H_2O \Rightarrow 2HCO_3^-$$
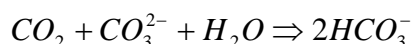
The net effect is removal of carbonate ions and production of bicarbonate ions (HCO$_3^-$) and a lowering in pH (Turley et al. 2004 and 2006). This in turn will encourage the dissolution of more calcium carbonate (CaCO$_3$). Indeed, the long-term sink for anthropogenic CO_2 is dilution in the oceans and reaction with carbonate sediments. The decline in carbonate ions will make it more difficult for calcifying organisms to form biogenic calcium carbonate and it is predicted that that this situation will continue for 100's of years (Kleypas et al. 1999; Broecker & Peng 1979; Feely et al. 2004; Orr et al. 2005b). Organisms form their calcium carbonate shells, tests or liths either in the form of calcite (e.g. coccolithophores) or the less stable form of aragonite (e.g. low latitude corals or pteropods). Orr et al. (2005b) highlighted their particular concern for high latitude calcifiers. Initially, the most vulnerable are species that form aragonite shells and live in high latitudes (polar and sub polar surface waters) where aragonite undersaturation will occur by around 2050 (at around 2 x CO_2, equivalent to 560 ppm). Those that form calcite shells and live in high latitudes will become increasing vulnerable after a further 50-100 years as calcite becomes undersaturated.

For example, the shallowing of the aragonite saturation horizon in the Southern Ocean is likely to have serious consequences on the aragonite shell producing pteropods which are the dominant calcifiers in these waters and a key food resource for higher organisms, including zooplankton, fish

(including commercial fish such as salmon, mackerel, herring, cod) and baleen whales. Marked dissolution of shells of living pteropods were found when incubated for only two days at concentrations of CO_2 predicted to occur in 2100 (Orr et al. 2005b). The authors asked the question of whether these key organisms can survive in these waters in the future and indeed whether they can shift their range to warmer, lower latitude waters that remain supersaturated in aragonite. Pteropods also dominate the flux of carbonate and/or organic carbonate from the surface of the ocean in the Ross Sea and South of the Polar Front (Orr et al. 2005b). Loss of these organisms may therefore impact the biological pump and removal of carbon from the surface of the ocean.

The calcifying phytoplankton group, the coccolithophores play a varied and complex role in the global carbon cycle and are thought to be the most important calcite producer on the planet. They produce calcite platelets or liths and their blooms can cover 100,000's of square km (Holligan et al., 1993). Reduced calcification in cultures of two species of coccolithophores has been observed when grown at 750 ppm CO_2 (Riebesell et al. 2000). A reduction in coccolithophorid global coverage may decrease flux of CO_2 to the atmosphere through reduced calcification, decrease flux to the sea through decreased primary production (although other organisms may replace them) and decrease ballast and thus removal of carbon from the surface ocean. The combined impacts are uncertain (Chuck et al. 2005) as are the consequences on the rest of the marine food web. Other non-calcifying organisms may grow in their place and impact the structure and processes occurring in the whole ecosystem. Impacts of high CO_2 on benthic calcareous organisms are dealt with below.

The sensitivity of calcifiers to acidosis and CO_2 varies among species depending on the degree of calcification and the calcite structure: If CO_2 was a key factor in the Perm-Trias Mass mass extinction, the stronger, but more sensitively calcificated corals, bryozoans and echinoderms were especially affected, while molluscs, arthropods including crustaceans as well as the chordates reacted less strongly (Knoll et al., 1996). It remains unclear whether crustaceans, which also display CO_2 effects on calcification (Wickins, 1984), are more sensitive after moulting due to repeated demand for calcium and bicarbonates for mineralizing their exoskeleton. Generally, the CO_2-induced reduction of carbonate super-saturation in the water can weaken carbonate-containing skeleton structures and make them less resistant against physical and biological erosion. When pCO_2 increases, the existing calcium carbonate structures finally dissolve (e.g. Bamber, 1987; Shirayama, 1995). These disturbances, also caused by lowered pH, are combined with a reduction of growth and reproduction (Bamber, 1987, 1990, Michaelidis et al., 2005).

CO_2 effects on phytoplankton already start when the CO_2 concentration is slightly increased, and such effects seem to have already played a role in the course of corresponding CO_2 variations in earth's history. Barker and Elderfield (2002) showed that CO_2 variations in the ice ages and inter-ice ages of the latest 50000 years correlated with the shell weights of fossil planktic foraminifers. These observations prove that marine calcification is already influenced by small fluctuations in atmospheric CO_2 values. Therefore, effects will progressively intensify with increasing CO_2 values. The capacity of sea water buffers to reduce pH alterations decreases with increasing CO_2 accumulation in the ocean. As a consequence less CO_2 is stored (cf. Fung et al., 2005) and biological effects increase more strongly.

4.2   Primary production and phytoplankton

Around half of global primary production is carried out by microscopic plants, the phytoplankton, which grow and die within a matter of days (Field et al. 1998). Their response to changing environmental conditions can therefore be very rapid. They also provide 99% of the organic matter used by marine food webs. A decline in oceanic primary production, either through reduced photosynthesis or through being less effective at nutrient uptake would have consequences on the rest of the food web. The Royal Society (2005) concluded that unlike land plants, most marine phytoplankton are thought to have mechanisms to actively concentrate CO_2 so that changes in seawater pH and CO_2 have little (<10%) if any direct effect on their growth rate or their elemental composition (Burkhardt et al. 1999; Gervais and Riebesell 2001; Beardall and Raven 2004;

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Schippers et al. 2004; Giordano et al. 2005). Although some studies have shown a change in the C:N:P composition in response to increasing CO_2 with large species-specific differences this may not have a significant effect on the global carbon cycle (Burkhardt and Riebesell 1997; Burkhardt et al. 1999). However, whilst taxon specific differences in CO_2 sensitivity have been observed in laboratory culture (Rost et al. 2003) it is currently unknown whether a reduction of the advantage of possessing a CO_2 concentrating mechanism will impact phytoplankton species diversity in the natural environment. This is a possibility and, should it occur, may impact the contribution of different functional group, primary production, food web structure and marine biogeochemical cycles. Exceptionally the coccolithophore, *Emiliania huxleyi,* increased its rate of photosynthesis in elevated CO_2 (Rost and Riebesell 2004). Considering it was also observed to decrease its rate of calcification at higher CO_2 (Engel et al. 2005) it is unsure whether this may offset the organisms directly benefit from increasing CO_2 (Riebesell et al. 2000). The Royal Society (2005) reported that most of the experiments on marine phytoplankton have been short term and did not provide sufficient time for any genetic modification that might enable them to adapt, some were carried out by artificially altering pH and therefore do not mimic the situation in the real world or were at pH's unlikely to be seen in future scenarios.

Nutrients such as nitrogen, phosphorus and iron often limit phytoplankton growth in major parts of the World's oceans. The lower pH expected over the next 100 years can theoretically impact the speciation of many elements (including oxidation states) (Zeebe and Wolf-Gladrow 2001; Turley et al. 2004). These include key nutrients (N, P, Si) and micronutrients (Fe, Co, Mn etc). For instance, a decrease in pH of 0,3 units could reduce the fraction of NH_3 by around 50% (Raven 1986). In contrast, the proportion of soluble iron may increase which might be beneficial to the 10% of the oceans where iron is thought to limit primary production. Clearly, unravelling the combined impacts of declining pH on nutrient concentration and speciation, on nutrient uptake by natural phytoplankton assemblages, their primary production or their nutritional value to the organisms that feed on them will be a challenge.

While the majority of primary production is carried out by microscopic planktonic algae, benthic primary producers play a key role in coastal areas providing habitats and breeding grounds and reducing coastal erosion through the dissipation of wave action. The Royal Society (2005) concluded that there was little data on the consequences of higher CO_2 concentrations on the photosynthetic or growth rates or composition of seaweeds or seagrasses although data available did indicate increased rates of photosynthesis at CO_2 concentrations higher than present (Beer et al. 2002). This may be because they may take up CO_2 by diffusion rather than through a concentrating mechanism. Kubler et al. (1999) found significant increases in the growth rate of a red seaweed at double today's concentration of CO_2. However, elevated CO_2 inhibited calcification in the coralline seaweed, *Corallina pilulifera* (Gao et al. 1993).

4.3 Microheterotrophic processes and bacteria, archaea and the microbial loop

Non-photosynthetic bacteria and archaea are important components of the marine environment and play a key role in major biogeochemical processes (e.g. decomposition of organic matter, nutrient regeneration, carbon remineralization and biogas production) and are an important food resource for small heterotrophic zooplankton and benthic detrital and suspension feeders (Azam et al. 1983). The main source of energy for planktonic heterotrophic bacteria is dissolved organic carbon released by phytoplankton. Phytoplankton production of organic carbon may change in high CO_2 waters (Engel et al. 2004) and if this occurs it seems likely that bacteria would respond rapidly to their main energy source. Bacteria also require nutrients for their growth and compete with phytoplankton for a range of nutrients. Any change in the speciation and supply of nutrients will also affect these groups of micro-organisms. We can find no data on the impacts of low pH/high CO_2 on elements of the microbial loop or bacteria-phytoplankton interactions. There is an urgent need to invest in our understanding of the impacts of a high CO_2 world on this fundamental part of the foodweb that drives so many key processes.

Coffin et al. (2004) investigating the potential impacts of direct deep ocean sequestration found that bacterial production rates were reduced in elevated CO_2 while Takeuchi et al. (unpublished) found potential activities of bacterial ectoenzymes and bacterial biodiversity were sensitive to

elevated CO_2. However, there is little information available on the effect of CO_2 concentrations due to ocean uptake of anthropogenic atmospheric CO_2 on surface ocean heterotrophic bacteria. Experiments carried out in the Bergen mesocosms may soon reveal CO_2 induced changes in their diversity (M Muhling, PML, unpublished).

Huesemann et al. (2002) found rates of nitrification were reduced by ~ 50% at pH 7 with inhibition at pH 6. This may result in a reduction of ammonia oxidation rates, the accumulation of ammonia instead of nitrate (that is, increasing the $NH_4:NO_3$ ratio). Depending on the nutrient requirements and uptake abilities of different species this has the potential to impact the growth and biodiversity of phytoplankton and bacteria. It should be noted that these pH levels are far lower than those predicted by ocean uptake of atmospheric CO_2. Further research is required on the impact of more realistic decreases (of 0,4-0,8 pH units from pre-industrial levels) in pH on nitrification. Also see section 4.6.

4.4   Secondary production, larval settlement and zooplankton

Impacts of high CO_2 and low pH on calcifying phytoplankton (such as the coccolithophores), zooplankton (such as pteropods) and heterotrophic micro-organisms (bacteria and archaea) and key biogeochemical processes are dealt with above. However, most benthic fauna have a planktonic larval phase to enhance their dispersal.

Larval settlement is a driver in the distribution and abundance of benthic populations (Gaines and Roughgarden 1985). Planktonic larval behaviour is important in the transport, delivery and settlement to the benthos and their response to changing environmental conditions may have a substantial effect on their settlement (Annis 2005). Juvenile forms of calcareous organisms may be less tolerant to changes in pH than adults. Indeed, greater than 98% of the mortality of settling marine bivalves occurs within the first few days or weeks after settling (Green et al. 2004). This is thought to be in part due to their sensitivity to the carbonate saturation state at the sediment-water interface. Compared to controls larvae of sea urchins grown at pH 7.8 (+500ppm) were smaller and those grown at pH 7.6 were also deformed (Kurihara and Shirayama 2004; Kurihara et al. 2004a). The authors postulate that this may be due to reduced rates of calcification of their calcium carbonate shells. The higher seawater CO_2 concentrations that will occur in the future may therefore enhance shell dissolution and impact recruitment success and juvenile survival.

Experiments associated with the concept of ocean sequestration of CO_2 have revealed the oceanic zooplankton (Adams et al. 1997; Yamada and Ikeda 1999) including those inhabiting the deep-sea (Watanabe et al. 2001) are sensitive to low pH. Sub-lethal effects on marine planktonic copepods may also be of concern including egg production rate and early development (Kurihara et al. 2004b). Foraminifera in the geological past have been sensitive to changes in oceanic pH, for example 55 Mya during the Palaeocene/Eocene thermal maximum (PETM) when ocean pH declined due to excessive CO_2 probably caused by release of methane hydrates (Zachos et al.). The shell weight of *Orbulina univera*, a planktonic foraminifer, was reduced under elevated CO_2 (Bijma et al. 2002).

However, further research is required in this area using pH values reflecting those predicted to occur through ocean uptake of anthropogenic CO_2 rather than the lower pH levels predicted from ocean disposal. Kurihara and Shirayama (2004) also call for experiments using CO_2, rather than acid, to reduce pH as there is higher sensitivity to high CO_2.

4.5   Water-breathing animals

4.5.1   *Direct effects*

Present knowledge can already negate any conjecture that higher life forms like animals may only be affected by CO_2 enrichment through the food chain. In water-breathing animals processes like calcification, growth, reproduction and activity are directly affected by increased CO_2 partial pressures. Effects already set in with an increase to 560 µatm (see below). The principle question is whether these most complex life forms, animals, may be most sensitive to these disturbances in similar ways as they are most sensitive to temperature (Pörtner, 2002)? Further knowledge needs

to be developed to answer this question. Effects on animals are also in the foreground when evaluating scenarios of CO$_2$ dumping or leakage in the deep ocean.

Disturbances of respiration, narcosis and mortality are short-term effects on animals in case of strongly increased CO$_2$ concentrations. Lower concentrations of CO$_2$ can, however, cause long-term effects which remain sublethal at first and affect processes like muscular activity, behaviour, growth, reproduction and finally life spans, with corresponding consequences at the level of population and ecosystem. There are also specific sensitivities in different life stages like eggs, larvae and juveniles. Juvenile stages are usually more sensitive than the adults (Pörtner et al., 2005d). Long-term effects beyond the duration of a reproduction cycle or individual lifespan are likely to be overlooked, but can finally have drastic effects on an ecosystem. Unifying mechanisms of CO$_2$ effects can be studied in animals from the intertidal zone, because these organisms even survive higher contents for a long time. Some of the invertebrates and fish examined up to now, however, live at depths below 2000 m or in permanently cold waters (e.g. Langenbuch und Pörtner, 2003, 2004), so that preliminary statements regarding effects on the physiology of animals in deeper or polar waters seem possible.

At first the sensitivity against increased CO$_2$ values was attributed to acidification (lowering of water pH) (cf. Shirayama, 1995, Auerbach et al., 1997). Specific effects by CO$_2$ and bicarbonate, however, must be considered in a complete analysis (Pörtner und Reipschläger, 1996). At least on short time scales there are considerable differences between experiments in which the same degree of acidification was either caused by hydrochloric acid alone (CO$_2$ released from carbonates was removed by aeration) or by increasing the CO$_2$ partial pressure. Only under CO$_2$ an immediate mortality of fish larvae was observed (Ishimatsu et al., 2004). In sea water acidified by hydrochloric acid (with a constant pCO$_2$) damages developed over longer periods. One reason certainly is that the highly diffusive CO$_2$ rapidly enters the body fluids via all epithelia and disperses into all body compartments. This internal accumulation of CO$_2$ causes most of the effects observed in animals (reviewed by Pörtner und Reipschläger, 1996, Seibel und Walsh, 2001, Ishimatsu et al., 2004, 2005; Pörtner et al., 2004a, 2005d). The CO$_2$ concentration to which an organism is acclimated will influence its acute critical tolerance limit. The capacity for acclimatisation and associated shifts in tolerance limits, however, has not yet been examined.

In Teleostei and Elasmobranchii ventilation is not only stimulated by hypoxia but also through increased CO$_2$ concentrations (Burleson and Smatresk, 2000; McKendry et al., 2001, McKenzie et al., 2002), with consequences for the energy budget of animals, i.e. the distribution of metabolic energy among energy consumers in the animal. Due to low CO$_2$ gradients between organism and water, water-breathing animals have a limited capacity to compensate disturbances in acid-base status by ventilation (Scheid, 1989). Upon ambient CO$_2$ accumulation an increase in CO$_2$ content in the organism cannot be avoided. Therefore, water-breathing animals nearly always use ion exchange mechanisms to compensate for hypercapnic disturbances of the acid-base status.

An increase in pCO$_2$ leads to acidification (the pH value decreases), and the content of bicarbonate increases, depending on the effect of other buffering substances (non-bicarbonate buffers), which are titrated by the increase in the content of carbonic acid. The decrease in pH is larger, and the increase of bicarbonate levels less in fluids with low buffering capacity. The passive increase in bicarbonate levels caused by the increase in pCO$_2$ is thus lower in sea water than in extracellular body fluids, and here considerably lower than in the intracellular space. Conversely, the strongest decrease is in sea water pH due to small quantities of non-bicarbonate buffers and the smallest decrease occurs in intracellular pH due to non-bicarbonate buffer values about five times higher than in the extracellular space. In most animals, invertebrates and vertebrates, the extracellular pH value is set at 0,5-0,8 pH units above the intracellular pH value (with the exception of squid and other cephalopods, here, intra- and extracellular pH values are nearly the same in many cases). Consequently, there are usually higher bicarbonate concentrations in extracellular than in intracellular space.

There have been many analyses of CO$_2$ effects on acid-base regulation of animals (Egginton et al. 1999), but only in few species were these combined with metabolic analyses (e.g. Reipschläger et al., 1997). Changes in metabolic rate are caused by changes in acid-base parameters (e.g. pH,

bicarbonates) in one or more body compartments (Pörtner and Reipschläger, 1996, Pörtner et al., 2000, Langenbuch and Pörtner, 2002). The processes of transmembrane ion regulation react to respiratory or metabolic acid loads or to changes in the acid-base status so that new acid-base equilibria develop, which are associated with shifts in e.g. the pH value. In marine fish transfer of acid-base equivalents are always connected with disturbances in osmotic regulation (salt-water balance), because of the required intake of counter-ions, which leads to an additional up to 10 % higher load of sodium chloride (Evans, 1984). A strong relation between acid-base status and ion regulation was also found in decapod crustaceans. Compensation of CO_2-induced acidification causes large and possibly unfavourable changes in the ion composition of plasma and other body fluids (Cameron und Iwama, 1989, Whiteley et al., 2001).

In all animals examined up to now, hypercapnic disturbances of acid-base status are compensated for by accumulation of bicarbonate-anions (Heisler, 1986b, Pörtner et al., 1998, Wheatly, 1989). This happens very effectively in the intracellular, but not always as effectively in the extracellular compartment. In fish, compensation in both compartments often is nearly complete (Larsen et al., 1997), while extracellular pH reaches the control value more slowly than intracellular pH, together with a slower increase in extracellular bicarbonate content (Heisler, 1986a). In contrast to many fish species, extracellular pH in marine invertebrates usually does not completely return to its original value. For example, compensation is by only 30 % in a marine worm (Pörtner et al., 1998) and is near 0% in *Mytilus galloprovincialis* (Michaelidis et al. 2005). A limiting factor for the extent of compensation could be, how much bicarbonate is available from the surrounding medium for extracellular compensation or from the extracellular fluid (blood, haemolymph) for intracellular compensation (Heisler, 1993; Pörtner et al., 1998). The newly established pH values affect transmembrane ion exchange mechanisms (Pörtner et al. 2000), oxygen transport and metabolic equilibria, which are important for growth or modulate the concentrations of neurotransmitters. An overview figure of CO_2 effects and affected mechanisms is given in Pörtner et al. (2005d). Based on these effects we expect that functional rates of the respective mechanisms as well as oxygen or energy turnover are mostly suppressed by high CO_2 and low pH values. Decreasing rates of protein synthesis affect functions like growth and reproduction (Langenbuch und Pörtner 2002, 2003). Finally, mortality increases (Kikkawa et al., 2004, Langenbuch und Pörtner, 2004), however, factors causing mortality are only known for acute effects of high CO_2 levels but not those causing mortality after long term exposure to moderately elevated CO_2 levels.

Many of these results were found in CO_2 concentrations which exceed by far those levels expected by 2100. Accordingly, further investigations are necessary to elaborate the potential influence of future atmospheric CO_2 levels on fish and other marine resources. Based on present knowledge, it cannot be excluded that marine living resources will diminish due to the generally depressing effect of CO_2 on physiological performances. However, no generalized statement on the extent of this depression can yet be made.

4.5.2 Short- and long-term effects of CO_2 in animals

To be able to assess the significance of CO_2 effects and affected processes at ecosystem levels, we must find out the advantages of effective acid-base regulation and the effects which changes in the acid-base parameters have under stress due to new environmental conditions, e.g. in case of increased CO_2 concentrations. Furthermore, CO_2 affects animals through physiological processes which differ depending on concentration and time scale (Pörtner et al., 2005d). It is possible that not all of these effects are elicited via disturbances in the acid-base status. The sensitivity against CO_2 also depends on lifestyle and energy turnover of the animals as well as on the physiological-functional characteristics of the respective phylum. Benthic animals show lower energy turnover than pelagic animals and may therefore be less sensitive. Especially in the tidal zone they are more adapted to variable environmental conditions like hypoxia, hypercapnia or extreme temperatures. Squid, however, are especially sensitive cephalopods, last not least because of their metabolic rate which is considerably higher than that of e.g. fish. The most active squid live in the pelagic areas of the open oceans and show levels of activity comparable to those of fish of similar size (O´Dor und Webber, 1986). The squid's high demand for oxygen is explained by their lifestyle

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and their cost-intensive swimming by jet propulsion (O´Dor und Webber, 1986). A similar understanding of CO_2 effects is not available for other organisms.

Acute sensitivities to CO_2, caused by effects on blood gas transport, are only important in scenarios in which CO_2 is discharged into the sea and can locally reach very high concentrations. Acute effects (within minutes or hours) mainly occur in response to high CO_2 concentrations and are to be considered near volcanic sources of CO_2 or during CO_2 disposal in the deep ocean. For many groups of animals it has been known for a long time that strongly increased CO_2 concentrations can cause acute decreases in metabolic rate or even anaesthesia. This is also confirmed by investigations of deep-sea fish (Tamburri et al., 2000). The acute sensitivity of some squid against increased CO_2 concentrations is due to the extreme dependence of oxygen transport by the extracellular pigment haemocyanin on well controlled changes in pH between arterial and venous blood. Such high pH sensitivity of haemocyanin can be explained by limited haemocyanin levels and the necessity to make maximum use of blood bound oxygen transport. Only in case of exactly controlled variations in blood pH, the pigment is loaded with oxygen at the gills and discharged completely in tissues (Pörtner, 1990, 1994). Of course, this system is very sensitive to CO_2 and the resulting pH disturbances (Pörtner und Zielinski, 1998).

Accordingly, the number of species showing acute sensitivity already in case of relatively low CO_2 concentrations of several thousand ppm is relatively small. In *Illex illecebrosus* a moderate decrease of the pH value by 0,15 pH units, caused by an increase in pCO_2 over 2 000 µatm, would limit oxygen availability to tissues and lower the capacity to use aerobic metabolism, i.e. aerobic scope. In case of a stronger increase of pCO_2 over 6 700 µatm a decrease of arterial blood pH by approx. 0,25 pH units is to be expected. This would lower oxygen binding capacity by approx. 50 % and possibly cause death by suffocation (Pörtner und Reipschläger, 1996). Other squid like *Loligo pealei* die at CO_2 partial pressures of 26 500 µatm (ppm), for similar reasons (Redfield and Goodkind, 1929). In fish the acutely effective concentration of CO_2 (after 72 h) is even higher, at 30 000 to 50 000 ppm (µatm, Crocker and Cech, 1996, Ishimatsu et al., 2004). Sensitivity is increased in early life stages (eggs, sperm, larvae, juveniles) (Crocker and Cech, 1996, Ingermann et al., 2002; Kikkawa et al., 2003, Ishimatsu et al. 2004), which display lethal limits at between 13 000 and 28 000 ppm in fish larvae.

Compared to squid, fish are much more protected against CO_2 effects due to their functional characteristics. They have a lower metabolic rate, a venous oxygen reserve and, above all, their haemoglobin is available at high concentrations in blood cells (erythrocytes) and is thus highly protected from disturbances of extracellular pH, mostly due to the high capacity of intracellular pH regulation. Compared to marine invertebrates, the fish's capacity to (nearly) fully compensate for an extracellular acidosis is generally much more developed. Accordingly, it is not the disruption of oxygen transport by the pigment, but rather the disturbance of cardio-circulatory function system which are finally lethal at high CO_2 levels in fish (Ishimatsu et al., 2004).

The general conclusion that the number of acutely sensitive animals is rather small is, however, debatable, especially if CO_2 levels increase in the deep sea. In fact, some deep-sea animals show a rather strong dependency of oxygen transport on pH, combined with a high oxygen affinity of their respiratory pigments. Seibel and Walsh (2001) therefore postulated that deep-sea animals, e.g. fish, would experience severe insufficiency in oxygen transport under increased CO_2 concentrations. However, their examples include organisms from the oxygen minimum layer at intermediate depths, like the mysid *Gnathophausia ingens* or some fish species (Childress and Seibel, 1998; Sanders and Childress, 1990). These species are adapted to ambient hypoxia and neither typical for the deep sea nor for other groups of fish.

Antarctic animals are more suitable animal models for deep sea organisms. Also, blood oxygen transport in Arctic cephalopods (e. g. octopods) is dependent on pH, but the pH-dependent regulation of oxygen transport becomes less important at reduced activity levels and decreasing temperatures (Zielinski et al., 2001). Nevertheless, this indicates that groups may react sensitively to increased CO_2 concentrations even in the cold. In Antarctic fish, however, the role of oxygen transport via haemoglobin is strongly reduced, compared to fish from warmer areas. The concentration of haemoglobin is lower, oxygen transport by the pigment is less dependent on pH.

These results comply with lower levels of motor activity in cold oxygen-rich waters (Wells et al., 1980, D`Avino and DeLuca, 2000; Tamburrini et al., 1998). These characteristics resemble those of deep-sea fish (from oxygen-richer regions below the oxygen minimum layer), where Graham et al. (1985) also found low contents of haemoglobin. Generally, fish (and squid) below 300 - 400 m lead an energy-saving, rather passive life (Childress, 1995; Seibel et al., 1997), which makes them less sensitive to acute effects of CO_2.

CO_2 effects on long time scales (weeks, months, years), however, are also to be expected for many other groups of animals and even at CO_2 concentrations which will be reached in the near future during continuing anthropogenic CO_2 release and adsorption into ocean surface waters. This was already explained for effects on calcification (4.1.). Accordingly, long-term investigations under moderately increased CO_2 concentrations are required for a better understanding of affected mechanisms and to understand and quantify ecological effects.

Animals that are not dependent on calcification processes also react to long-lasting increases in CO_2 concentrations. In *Sipunculus nudus* CO_2 causes a long-term suppression of aerobic energy turnover. The degree of depression depended on concentration and reached up to 35 % at 20 000 µatm pCO_2 (water pH ~ 6.6). Unter normo- as well as under hypercapnia the non-compensated acidosis in the extracellular space could be identified as one cause of the decrement in metabolic rate (Reipschläger and Pörtner, 1996). In parallel with the decrease in extracellular pH the transmembrane exchange rate of proton-equivalent ions fell, consequently, less natrium was pumped through the Na^+/K^+-ATPase, thereby lowering the energy demand of acid-base regulation (Pörtner et al., 2000).

Further study showed, however, that the modulation of acid-base regulation cannot fully explain the suppression of metabolic rate. Ventilation is also reduced under hypercapnia, indicating that a central nervous mechanism is involved (Pörtner et al., 1998). In fact, an accumulation of the neurotransmitter adenosine occurred in the nervous tissue of *S. nudus* under CO_2. Infusions of adenosine caused a suppression of metabolism (Reipschläger et al., 1997). Similar effects were also found in some vertebrates under anoxia (e.g. freshwater fish and turtles) (Lutz and Nilsson, 1997). The role of adenosine or other neurotransmitters in marine fish under hypercapnia still requires investigation.

Further results show an increasing degradation of protein under hypercapnia. At the same time the rate of protein synthesis fell (Langenbuch and Pörtner, 2002), as a major process contributing to growth and reproduction. This effect would explain the decrease in growth seen in mussels under hypercapnia (Michaelidis et al., 2005). Reduced growth rates were also found in crustaceans and fish. Many marine fish, however, react differently to hypercapnia than marine invertebrates, because their metabolic rate is not slowed down, and at the same time ventilation rate may increase. Considering the high energy cost of ventilation in water breathers the associated shift in energy budget can explain the observed reduction of growth.

In animals from the intertidal zone the suppression of metabolic rate under CO_2 appears adaptive, because it helps to passively survive unfavourable environmental conditions. In the long term (after several weeks at 10 000 ppmv CO_2), however, increased mortality was observed in the sipunculid, with unclear cause and effect relationships (Langenbuch and Pörtner, 2004). Investigations in mussels from the Mediterranean Sea suggest that the effects on calcification as well as metabolic depression and the shift in energy allocation occur in parallel (Michaelidis et al., 2005). Consequently, both the slow-down of somatic growth as well as reduced calcification are involved in growth reduction. These effects are drastic, i.e. a growth reduction by more than 50 % was found in mussels kept under CO_2 at pH 7.3, a pH value expected for the year 2300. As mentioned above, other investigations already show a significant reduction of growth and survival in echinoderms and gastropods from the Pacific at CO_2 concentrations just 180 ppm (µatm) above today's values (section 4.1). As per present scenarios of increasing anthropogenic production of CO_2, such effects will already set in 10 - 20 years from now.

Long-term effects of hypercapnia are also to be expected in deep-sea organisms, with corresponding effects on geographic species distribution and their population structures. Their low

metabolic rate suggests that the capacities and efficiencies of cellular and organismic acid-base regulation are reduced compared to organisms from the photic zone (Seibel and Walsh, 2001). A lower intracellular buffer capacity (Seibel et al., 1997) and reduced rates of ion exchange at the gills (Goffredi and Childress, 2001) could be typical for deep-sea fauna, with the above mentioned consequences for acid-base, ion and metabolic equilibria. Reduced energy turnover rates and thus limitations of growth and reproduction would have to be expected on long time scales.

The conclusion from previous investigations is that many organisms can tolerate CO_2-induced acidification to pH values of 7 to 6,5 for limited time, but a small increase of atmospheric CO_2 levels beyond today's values may already cause metabolic shifts in some animals (especially echinoderms, molluscs), associated with reduced rates of growth and reproduction as well as increasing mortality.

At first sight, the effects of CO_2 described here comply with a key role of CO_2 during mass mortality in Permian-Triassic mass extinctions (cf. Knoll et al., 1996). Here pCO_2 values are postulated for the surface layers of the seas, which correspond to those reached locally in CO_2 discharge scenarios. However, the hypothesis of Knoll et al., that mainly animals without gills and with low capacity of circulation and low metabolic rates have been affected, is not supported by the physiological findings discussed here. As explained above, ventilatory compensation plays a small role in more active water breathers. It rather seems to be the extent of calcification, the sensitivity of skeleton structures and the dependence of organismic functions on calcified structures, e.g. in echinoderms, bryozoans and corals which contributes to increased CO_2 sensitivity of these organisms.

4.6   Benthic biogeochemistry and fauna

With increasing CO_2 and declining seawater pH the average carbonate saturation state of shallow sea sediment pore waters could decline significantly, inducing dissolution of metastable carbonate phases within the pore-water-sediment system (Andersson et al. 2003). Shallow sea benthic ecosystems, such as in the North Sea, may be particularly sensitive to reducing seawater pH (Turley et al. 2006; The Royal Society 2005) as they are already characterised by strong geochemical gradients, including pH (Fenchel and Riedl 1970). Benthic communities have adapted to these gradients with different species occupying different depth horizons (Barnes and Hughes 1988) so even though benthic systems as a whole are already subject to a relatively large range in pH, many of the organisms and processes that exist within them are not. The surface layer is most densely inhabited, whilst only those species capable of oxygenating their immediate environment, for example through ventilated burrows, are able to dwell below the redox discontinuity depth (Furukawa 2001). Microbial communities and the processes they carry out (e.g. nitrification and denitrification) also differ considerably between the oxic surface sediments and the deeper anoxic layers. Consequently, animals which inhabit permanent burrows may have a greater tolerance to changes in pH than non-burrow builders.

Burrowing and bioturbating benthic organisms alter the physical and chemical characteristics of their immediate environment (Rhoads and Young 1970) and thereby the rate of nutrient flux at the sediment/water interface (Nedwell and Walker 1995; Banta et al. 1995; Widdicombe and Austen 1998; Howe et al. 2004) and the maintenance of biodiversity (Widdicombe et al. 2000). Some of these key "ecosystem engineers" have calcareous structures (e.g. heart urchins, sea urchins, starfish, brittle stars and molluscs) and may be particularly vulnerable to the decline in carbonate ions (see section 4.1). Sea urchins appear particularly susceptible even at CO_2 concentrations (550ppm) likely to be reached by around 2050 (Shirayama and Thornton, 2005). Even amongst such organisms which depend on calcium carbonate structures variability in tolerance has been observed with echinoderms showing less tolerance to pH change than molluscs (Shirayama et al. 2004). This potential difference in pH tolerance between benthic species could lead to the selection of more tolerant species and thereby substantial changes in the structure and function of sediment communities in the face of changing levels of pH. Although we are unaware of published work on impact of high CO_2 on benthic diversity and ecosystem function, work has just started on this at Plymouth Marine Laboratory.

Pelagic and benthic ecosystems are closely coupled, even in the deep ocean seas (Turley 2000). Sinking particles produced initially by primary production in the photic zone act as the main food resource for sediment dwelling organisms. In shallow coastal seas, up to 80% of the nitrogen required by photosynthesis comes from microbial regeneration of organic matter within sediments (Dale and Prego 2002). Changes to the rate of benthic regeneration of nutrients through changes in the benthic species composition and their function could therefore impact pelagic production. Conversely, changes to rates of primary production, the composition of the primary producers and the rate and timing of their flux to the sea bed could impact the food resources for the sediment dwellers and nutrient regeneration. Also see "Biological pump" (section 4.7).

Decreasing pH is likely to result in changes to the speciation and oxidation states of metals (Turley et al. 2004; 2006 and refs therein). Theoretical models predict that decreasing pH generally increases the proportion of free dissolved metal species by reducing the concentration of particulate, immobile metal species. In lakes, a decline in pH from 8 to 6 increased the percentage of free copper from 3 to 73% (Morel et al. 1975). It is generally thought that the free dissolved form of metals have a higher toxicity than particulate forms when present at high concentrations (e.g. copper and zinc). A decrease in pH may also change the nature and form of particle surfaces and therefore metal partitioning (Mouvet and Bourg 1983) such that there may be release of previously bound metals from the sediment to the seawater. This could be of particular importance in shallow seas with high sediment loadings of bound metals but we are unaware of current research in this area. In vast areas of the open ocean primary production is limited by iron (Coale et al. 1996; Boyd et al. 2000). Theoretically, lower pH could make iron more bioavailable through changing its speciation and thereby reduce its limitation to phytoplankton growth in these regions (Morel et al. 2001; Turley et al. 2004).

4.7 The biological pump, carbon flux and delivery of food to the benthos

The global ocean sink for anthropogenic CO_2 is thought to be around half of that produced by human activities since pre-industrial times (Sabine et al. 2004). Organisms fix and export carbon to the deep sea, either as organic carbon (the organic carbon pump which causes a net draw down of CO_2 from the atmosphere into the oceans) or as calcium carbonate (the carbonate counter pump which causes a net release of CO_2 to the atmosphere). The ratio between these two processes (the rain-ratio) determines the flux of CO_2 between the surface ocean and the atmosphere (Riebesell 2004). This biological pump is an important part of the global carbon cycle as over long time scales calcium carbonate is the major form in which carbon is buried in marine sediments (Royal Society 2005). The substantial and rapid changes to the carbonate chemistry of the system may affect plankton species composition by inhibiting calcifying organisms such as coccolithophores, pteropods, gastropods, foraminifera and corals in waters with high CO_2 (Riebesell 2004; Engel et al. 2005; Orr et al. 2005; Royal Society 2005). Engel et al. (2004) reported increased transparent exopolymer particle (TEP) production with elevated CO_2. Since TEP enhances aggregation of cells its increased production could increase the biological pump while decreased calcification by planktonic organisms would reduce the input of ballast and the rate of sinking (Klaas and Archer 2002). Mesocosm experiments of a bloom dominated by *E. huxleyi* indicated that at CO_2 concentrations predicted for 2100 there was a delay in the onset of calcification, a 40% reduction in net community calcification and enhanced loss of organic carbon from the water column implying a shift in the rain ratio (Delille et al. 2005). The behaviour of key calcifiers to higher CO_2 concentrations will determine the future strength of the biological pump (Riebesell 2004), the delivery of food to deeper waters and to benthic organisms (Turley 2000), the global carbon cycle and climate regulation (Archer and Maier-Reimer 1994). Also see section 4.6.

4.8 Adaptation

Assuming the IPCC (2002) predicted concentration of atmospheric CO_2, the changes in seawater chemistry that will occur by 2100 or even by 2050 could well influence the structure of marine ecosystems, their biodiversity and impact many trophic levels. Phenotypic adaptations to raised CO_2 over multiple generations needs to be studied (Collins and Bell 2004) under natural

environmental conditions (Royal Society 2005). The outstanding question is whether organisms and ecosystems can adapt to these rapid and challenging environmental changes.

5. Other changes to marine systems and their synergistic impacts

Apart from ocean acidification, other important changes to the oceans are predicted to occur over the same period of time which could have synergistic impacts on marine ecosystems. Surface water temperature is already increasing and predicted to increase further, accompanied by changes in ocean carbon cycling (Denman et al. 1996; Boyd and Doney 2003) while changes in rainfall and land run off will impact salinity and nutrient input to coastal seas. Increases in temperature (and salinity) will increase the degree of stratification of the water column (unless currents and wind mixing increase to balance this). Increases in temperature, stratification and nutrient input from land run-off could increase the potential risk of hypoxia or anoxia in shelf sea ecosystems. Increased stratification would reduce the influx of nutrients from below the thermocline that sustain primary production and the drawdown of CO_2. As the oceans, and organisms within them, are a major source of other atmosphere changing gases (Nightingale and Liss 2002) changes to the biology could impact their production and cycling.

The combined impact of ocean acidification and other global changes could well influence the relative composition, productivity, timing, location and predominance of the major functional groups of phytoplankton and zooplankton and thereby impact the rest of the food web. Models that consider the key interactions of these functional groups and their response to a high CO_2 world are key to making predictions of the overall impact on marine biogeochemical cycles and food webs (Boyd and Doney 2002; Legendre and Rivkin 2005; Turley et al. 2006). Experimentalists will need to consider multi-factorial impacts to help provide information to drive or test the models.

As discussed in section 4.5, the relative role of increased CO_2 and other environmental changes for the Permian-Triass mass extinction is debated. The analysis by Knoll et al. (1996) neglects the role of temperature and its variability which most probably contributed considerably to mass mortalities. In the marine realm, mass mortalities were often connected with strong, long-term and recurrent climate variations and especially with cooling events (Stanley, 1987, Ivany et al., 2000, Pörtner, 2001, 2004). In this context it is important that, according to the principle of oxygen-limited temperature tolerance, the animals' thermal tolerance window is determined by the integrated capacity of ventilatory and cardio-circulatory functions for the uptake and distribution of oxygen in the body (Pörtner, 2001, 2002). This capacity is increased in cold-adapted eurytherms, combined with an increase in energy turnover. The question arises whether CO_2 might influence these relationships.

A recent analysis of the marine fossil record showed that mass mortalities repeatedly led to a drastic increase of the fraction of mobile animals in the marine fauna (water breathers) (Bambach et al., 2002). This pattern shows that the most active marine animals survived. According to the concept of oxygen-limited temperature tolerance, the most active animals are those which are especially cold-eurytherm, i.e. tolerant to large temperature variability (Pörtner 2002b, 2004). The most active and eurytherm animals are also those with the highest energy turnover. This effect is to be expected in a similar way in all taxa. CO_2 accumulation and hypoxia alone cannot have caused these effects, because they have a depressing effect on many physiological rates and favour those forms which survive in hypoxic and hypercapnic surroundings at low rates of energy turnover. This would rather lead us to expect the opposite, survival of the less active. However, if there were extreme variations in temperature at the same time, CO_2 enrichment and hypoxia could have influenced the extent of eurythermy and thus have exacerbated mass mortality so that only the most eurythermal animals survived.

This hypothesis is supported by the extant significance of interactions between temperature, CO_2 enrichment and hypoxia in marine ecosystems: The present anthropogenic warming and eutrophication trends are combined with a decrease in oxygen contents (hypoxia), especially in coastal zones. All three factors, warming, accumulation of CO_2 in surface layers and increasing hypoxia events combine in their effects on marine fauna. The depressing effect of CO_2 and hypoxia on the animal's aerobic capacity results in a narrowing of the thermal tolerance window,

i.e. in a higher sensitivity to extreme temperatures (Pörtner et al., 2005d). This would cause a decreasing range of biogeographical distribution in a climate gradient. Such effects will have a particularly negative influence on populations at the limit of their geographical distribution. Recent study confirms the narrowing of the temperature window under CO_2 (unpublished), quantitative statements, however, are not possible yet. These effects will concern stenotherms and also the most eurythermal animals, but the narrowing of their geographical distribution range may be less fatal, because they start from a larger area of distribution.

The negative interactions between temperature extremes and CO_2 are particularly acute in coral reefs. If the atmospheric CO_2 content stabilizes at 550 ppm, a marginalisation of these habitats is already impending (Hoegh-Guldberg, 2005). This would be the result of the combined burden by increased temperatures and CO_2. Increased temperatures are declared responsible for the (six) recurrent bleaching events since 1979. The endosymbiontic zooxanthellae leave their host, the coral bleaches. For the year 1998, the loss of live corals was estimated at 20% worldwide. The increase in CO_2 in parallel to warming trends leads to a decrease in the over-saturation degree of aragonite. This over-saturation is important for the velocity of the calcification process. Calcification is not only the basis for the growth of coral reefs, it also counteracts the erosion process. The CO_2-related slow-down of the calcification rate also hinders the retreat of coral reefs into cooler areas of the sea, so that, as per present perspectives, increased temperatures and CO_2 contents will drastically limit the distributional areas of today's coral reefs (Hoegh-Guldberg, 2005). A comparison with earth history raises the question of why coral reefs could exist e.g. in the Siluric in spite of high atmospheric CO_2 levels. At that time, the calcium contents in sea water were 2 to 2,5 times higher (Arp et al., 2001) and thus provided the required super-saturation values of carbonates.

Due to their specialization on a narrow temperature range, on aragonite saturation and on high concentrations of light, today's coral reefs are among the most endangered ecosystems. Nothing can be said, however, on the sensitivity of the insufficiently explored cold-water corals. Besides, there are potentially much endangered species in all ecosystems (Benthic infauna and epifauna and pelagic fauna), especially among echinoderms and pteropods. Changing composition of species communities due to warming are already being observed and might already be influenced synergistically by previous CO_2 accumulation in the ocean.

6.   Research priorities

The Royal Society (2005) recognised the seriousness of CO_2 induced acidification, the infancy of research in this area and recommended that a major international research effort should be launched on a scale to that expended on climate change. Key research areas highlighted in the report were the effects of enhanced atmospheric CO_2 on ocean chemistry and the resulting impacts on sensitive organisms, functional groups and ecosystems. The report recommended the need to focus on establishing a better understanding of the various metabolic processes at different parts of the life cycle and how these are expressed at the ecosystem level and developing models that include effects of pH over a range of scales from the level of the organism to that of the ecosystem and the need to include synergistic impacts with those of climate change.

The Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) project is an international and multi-disciplinary activity jointly sponsored by the International Geosphere-Biosphere Programme (IGBP) and the Scientific Committee on Oceanic Research (SCOR). The IMBER (http://www.imber.info/) project goal is to understand how interactions between marine biogeochemical cycles and ecosystems respond to and force global change. Ocean acidification is one of the global change priorities that IMBER recognises as important to address.

The Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO convened an open symposium on *The Ocean in a High-CO2 World* on 10-12 May 2004 in Paris, France at UNESCO Headquarters (http://ioc.unesco.org/iocweb/co2panel/HighOceanCO2.htm). The symposium participants identified the research agenda/priorities related to the ocean in a high-CO$_2$ world, without mitigation, with attention to both biogeochemical and organismal/ecological aspects. It therefore

represents a collective view of research priorities in this area. The following is taken from the report.

6.1 Forcing factors

The most obvious forcing factor on the ocean in a high-CO_2 world is increased atmospheric pCO_2, which will increase the surface ocean (and eventually deep ocean) pCO_2 and lower pH. A major research priority will be to conduct research and modelling that will allow predictions of changes in ocean carbonate chemistry, and on how these changes will differentially affect calcitic and aragonitic organisms. As pCO_2 is increasing, other environmental variables will also change as a result. For example, likely changes that will accompany increased pCO_2 include increased temperature, changes in availability of nutrients (due to changes in redox conditions, ocean mixing, patterns of precipitation, dust inputs, and increased stratification), decreased O_2 in the warmer water, changes in salinity due to heating and precipitation effects, and changes in ocean mixing, circulation and wind. It will be very important to consider, in research, observational, and modelling activities, how these changes interact to affect marine biogeochemical processes and feed back to the Earth system. It also will be important to consider regional differences and to consider the combined effects of higher pCO_2 levels, higher temperature, and low O_2 concentrations.

6.2 Ecological/organismal aspects

Keeping in mind the forcing factors described above, it will be necessary to conduct research on both ocean biology and biogeochemistry. In terms of biology, effects are naturally expected for calcifying organisms, but it is also important to study the effects of increasing ocean pCO_2 and associated environmental changes on non-calcifying organisms. Interactions and synergies among variables (e.g., pCO_2 and temperature) are particularly important. Specifically, research should include

- Effects on community structure and composition (including how species-specific responses will affect community composition), from bacteria to vertebrates.

- Effects on genetic diversity, species diversity, and the diversity of functional groups.

- Microevolutionary potential and rate of evolutionary change—Earth's temperature and atmospheric CO_2 concentrations have changed in the distant past, but not at the rapid pace that is now occurring, nor at the high CO_2 levels now encountered.

- Many organisms were probably able to evolve quickly enough to adapt to global changes in the past. Will they be able to adapt to the more rapid pace of change now occurring? Can adaptation occur under a continually and rapidly changing environment versus one that eventually stabilizes?

- Sub-lethal effects—Most effects are likely to be sub-lethal, including decreased reproductive potential, slower growth, and increased susceptibility to disease.

6.3 Key biogeochemical processes

Increasing surface ocean pCO_2 and decreasing pH can affect a variety of processes that are important in regulating the oceanic cycles of carbon, nitrogen, and other elements. New research is needed to understand how the ocean will respond to increasing atmospheric CO_2, particularly related to:

- Primary production—Will increasing pCO_2 in the surface ocean fertilize phytoplankton? If so, which species? What effects will this have on higher trophic levels? Since CO_2 generally is not a limiting resource for phytoplankton, production might not increase much, due to limitations in other elements. CO_2 fertilization may affect elemental stoichiometry (C/N/P).

- Remineralization—Auto- and heterotrophic processes are likely to respond differently to environmental changes (e.g., due to differences in temperature dependency). What effect will this have on the balance between primary production and remineralization?

- Will changes in nitrogen fixation, denitrification and nitrification be induced by changes in phytoplankton species composition and changes in oxygen levels?

- DOM transformations (aggregation, solubilization, biological turnover)—Will increasing pCO_2 change the proportion or type of carbon that enters the DOM pool? How will this affect the dynamics of dissolved organic material and particles?

- How does increasing pCO_2 impact the precipitation of $CaCO_3$ by planktonic and benthic calcifiers? What are the current dissolution kinetics of aragonite and calcite and how might they change under different scenarios of increased pCO_2? What impact will increasing pCO_2 and decreasing pH have on dissolution of $CaCO_3$ in the upper ocean, throughout the water column, and in ocean sediments? Will there be an impact on the $CaCO_3$ compensation depth?

- How will changes in the above processes affect export production and the rain ratio?

6.4   Key types of ecosystems/species to be investigated

Some ecosystems are more likely to be affected than others by increasing oceanic pCO_2 and decreasing pH, or may have more significant feedbacks to the Earth system. These ecosystems are priority areas for study:

- Ecosystems dominated by and/or structured by calcifying organisms such as coccolithophores, foraminifera, pteropods, and coral reefs (including different species and strains). There is some evidence that increasing pCO_2 would prevent the colonization of corals in new environments (within the temperature tolerance of the corals) because it will cause a decrease in the saturation of $CaCO_3$ in seawater.

- Ecosystems dominated by and/or structured by other biogeochemically relevant functional groups (pelagic and benthic) and "ecosystem engineers"/"keystone species".

- Intertidal and shallow subtidal areas.

- The mesopelagic zone.

- The Southern Ocean and subarctic Pacific Ocean.

6.5   Approaches

Discussion group participants identified a set of promising approaches to study how the ocean might respond in a high-CO_2 world. These approaches range from small-scale laboratory experiments to open-ocean perturbation studies:

- Laboratory experiments—Small-scale studies in the laboratory can help isolate various factors to increase the understanding of results from larger-scale field studies and to guide planning for mesocosm and field studies.

- Mesocosm experiments—Experiments in mesocosm enclosures have produced useful results about how species composition changes in carbon-altered ecosystems. These experiments make it possible to create experimental designs with replication and controls on a larger scale and more realistic conditions than in the laboratory. An important activity will be to design standard experimental protocols that will make these experiments more reproducible.

- Short-term open-ocean perturbation experiments—Large-scale open-ocean iron fertilization experiments have yielded significant new knowledge about ocean ecosystems in the past decade. Short-term additions of carbon dioxide to various

ecosystem types should result in similar information gains related to effects of carbon on the ocean.

- FACE-like experiments— Free Air CO_2 Enrichment (FACE) experiments are currently being conducted at many sites worldwide, in a variety of terrestrial, non-agricultural ecosystems. These experiments involve additions of carbon dioxide to research plots continuously for several years to maintain elevated atmospheric CO_2 levels that mimic levels that will be experienced under likely future scenarios. These experiments have demonstrated how plant communities will respond in both the short and long term. The continuity of these experiments is an important feature, because some long-term effects have been shown to differ from short-term effects on the same parameters. Both SOLAS and the IMBER project have proposed FACE-like experiments for the ocean. The benefit of such experiments is that they are more likely to show the actual long-term effects that will occur in the future. The major anticipated drawback is that it might be impossible to use for pelagic communities without enclosing them in some way or somehow using a Lagrangian approach. There is a need to start with a feasibility study because the amount of CO_2 or acid required for a full-scale pelagic FACE experiment may be very high. The other drawback is the public perception problem. This drawback might be approached by pointing out that the effects of elevated CO_2 under "business as usual" scenarios may be so severe that understanding them might cause policymakers to think more carefully about emission controls or other mitigation methods.

- Model development— Ongoing development of models should be pursued, to assess the role of climate feedback and elevated CO_2 levels on ocean ecosystems and biogeochemistry. This will require the reconsideration of the distinction between the euphotic zone and the underlying waters (above the permanent pycnocline). Models should consider the high-CO_2 world in an Earth system context, where feedbacks and indirect effects are important and are often the dominant drivers, and disciplinary distinctions between functional biodiversity, ecosystem functioning and the fluxes of elements and associated feedbacks are no longer appropriate.

Other important research and observation approaches that should be explored include:

- Encouraging experimentalists, field researchers, and modelers to work together.

- Using specific locations that are acid- or CO_2-rich due to human effects or natural factors (e.g., the Rio Tinto, outlets of power stations, and natural CO_2 vents such as on Loihi Seamount).

- Adding stable pH sensors to Argo profiling floats.

- Studying interactions between coastal areas and the open ocean, and between the seafloor and water column.

- Following-up on the symposium with international working groups to focus on specific implementation tasks, though SOLAS and IMBER, the International Ocean Carbon Coordination Project, and/or SCOR working groups.

6.6   Additional areas of research

The authors of this report to OSPAR BDC recognise additional areas of research since the above 2004 meeting. Impacts studies should also take into account the more subtle effects such as on intracellular processes, cell or metabolic efficiency and indirect effects such as their ability to compete for resources, cope with other environmental stressors, reproduce and adapt. They are:

- Impacts on zooplankton

- Impacts on predator-prey interactions

- Impacts on larval development, settlement and recruitment

- Impacts on primary and secondary production and remineralization

- Impacts on higher trophic groups such as sea mammals and birds

- Impacts on socio-economics including aquaculture and fisheries

- Impacts on services provided by marine systems

- Understanding past geological analogues

- What are the relative impacts of mitigation methods and how do these measure against non mitigation?

- What are the synergistic impacts of ocean acidification and other serious climate change variables

- Feedback to the Earth system

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