

# *The Ocean in a High CO<sub>2</sub> World*

AN INTERNATIONAL SCIENCE SYMPOSIUM.  
MAY 10-12, 2004  
UNESCO, PARIS, FRANCE

## **SYMPOSIUM ON THE OCEAN IN A HIGH-CO<sub>2</sub> WORLD PARIS 10-12 MAY 2004**

### **PROGRAMME AND ABSTRACTS**

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The Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) welcome you to the international science symposium, *The Ocean in a High-CO<sub>2</sub> World*. This symposium will address the biological and biogeochemical consequences of increasing atmospheric and oceanic CO<sub>2</sub> levels, and possible strategies for mitigating such increases. The symposium includes plenary presentations, discussion sessions on research priorities, and a poster session. Invited papers from the symposium will be published in a special issue of the *Journal of Geophysical Research-Oceans*, subject to normal peer-review procedures, and research priorities will be published separately for the benefit of ocean scientists and research program managers worldwide.

#### Sponsorship of the Symposium:

The SCOR/IOC Planning Committee for the symposium is grateful for the sponsorship of the Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO. Financial contributions, scientific oversight, and staff support from SCOR and IOC have been (and will continue to be) crucial for the success of this activity. The committee thanks IOC for hosting the symposium, supporting some of the local costs, and providing excellent staff support. Finally, we acknowledge grants from the U.S. National Science Foundation, Division of Ocean Sciences and the Research Council of Norway to SCOR for the symposium.



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## ORGANIZATION OF THE SYMPOSIUM

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### **SCOR/IOC Symposium Planning Committee**

Ralph Cicerone (Chair, USA)  
James Orr (Vice-Chair, France)  
Phil Boyd (New Zealand)  
Peter Brewer (USA)  
Peter Haugan (Norway)  
Jim McWilliams (USA)  
Liliane Merlivat (France)  
Takashi Ohsumi (Japan)  
Silvio Pantoja (Chile)  
Hans-Otto Poertner (Germany)

### **Symposium Coordinators:**

Maria Hood, Program Specialist, Oceans and Climate, IOC  
Ed Urban, Executive Director, SCOR

### **Assistance with Conference Preparation:**

Virginie Bonnet, IOC – logistics  
Elizabeth Gross, SCOR – logistics  
Phyllis Steiner, SCOR - registrations

## AN INTRODUCTION TO THE SYMPOSIUM

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### **Introduction**

The atmospheric concentration of carbon dioxide is now higher than experienced on Earth for at least the last 400,000 years, if not the last several million years, and is expected to continue to rise, leading to significant global temperature increases by the end of this century. It is now well established that there is a strong possibility that surface ocean pCO<sub>2</sub> levels will double over their pre-industrial values by the middle of this century, with accompanying surface ocean pH changes that are 3 times greater than those experienced during the transition from glacial to interglacial periods.

The ultimate objective of the United Nations Framework Convention on Climate Change (UNFCCC) is "to achieve stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system." While "dangerous anthropogenic interference with climate" has been widely discussed, no such debate has taken place over acceptable oceanic CO<sub>2</sub> levels. As a result, there are no standards to apply to judge what oceanic CO<sub>2</sub> levels should be considered tolerable for marine life, or how proposed carbon management strategies might moderate or exacerbate effects on ocean chemistry and biology.

Much discussion has been devoted to how to "sequester" some of the atmospheric carbon dioxide, in plant biomass, or stored in geologic structures or in the ocean. The ocean is absorbing approximately one-third of the carbon dioxide added to the atmosphere by human activities each year, and over the next millennium, will absorb approximately 90% of the CO<sub>2</sub> emitted to the atmosphere. The ocean is one of the largest natural reservoirs for carbon. Ocean strategies for sequestering atmospheric CO<sub>2</sub> involve enhancing the ocean's natural capacity to absorb and store atmospheric CO<sub>2</sub>, either by inducing and enhancing the growth of carbon-fixing plants in the surface ocean, or by speeding up the natural, surface-to-deep water transfer of dissolved CO<sub>2</sub> by directly injecting it into the deep ocean. However, although much relevant research has been conducted in the past decade, the potential effectiveness and risks of these forms of carbon sequestration in the ocean have not been thoroughly discussed and assessed, and even relatively small changes in CO<sub>2</sub> concentrations may have large negative impacts on marine life and natural biogeochemical cycles of the ocean.

### **The Ocean in a High-CO<sub>2</sub> World Symposium**

In order to assemble scientific information relevant to the issues of ocean carbon sequestration, the Scientific Committee on Oceanic Research (SCOR) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO have planned a symposium on The Ocean in a High-CO<sub>2</sub> World. The symposium will bring together ocean scientists to discuss the likely consequences of passive CO<sub>2</sub> absorption by the ocean in comparison with the potential consequences of purposeful ocean carbon sequestration activities. Topics will include both chemistry and biology, including the impacts of elevated CO<sub>2</sub> levels on marine life, the dissolution of calcium carbonate, and the impacts on coral reefs. It will also include evaluation of the possible benefits and impacts of surface fertilization and deep-ocean CO<sub>2</sub> injection strategies in their many forms. The symposium

will not determine whether it would be a good policy choice to sequester carbon dioxide in the ocean, but will determine what scientific information is available, and what is still needed, to make informed policy decisions.

The symposium papers will be published in a special issue of the *Journal of Geophysical Research-Oceans* and research priorities will be published separately for the benefit of ocean scientists and research program managers worldwide. The research priorities will be transmitted to the new international research projects (the Surface Ocean - Lower Atmosphere Study [SOLAS] and the Integrated Marine Biogeochemistry and Ecosystem Research [IMBER] project) for consideration, since both of these projects have major foci related to the ocean carbon cycle.

### **About the Sponsor Organizations**

SCOR is an international non-profit organization formed in 1957 to identify ocean research topics that would benefit from enhanced international action; it establishes working groups and other subsidiary bodies—either alone or in conjunction with other organizations—for detailed examination of problems related to the marine environment and international ocean science. SCOR also works with other international organizations to develop and sustain major international ocean research projects.

IOC is an intergovernmental organization formed in 1960 to "promote international cooperation and to coordinate programmes in research, services, and capacity-building, in order to learn about the nature and resources of the ocean and coastal areas and to apply that knowledge for the improvement of management, sustainable development, the protection of the marine environment, and the decision-making processes of its Member States." SCOR is a body of the International Council for Science (ICSU) and IOC is a body of the United Nations Educational, Scientific and Cultural Organization (UNESCO).

SCOR and IOC have been involved separately and together in activities related to the role of the ocean in the global carbon cycle since 1960. Roger Revelle played a leading role in establishing both IOC and SCOR. A UNESCO conference convened by Revelle led to the creation of IOC, modelled after the World Meteorological Organization. In 1960, SCOR Working Group 2 focused on Carbon Dioxide in the Ocean. In 1979, recognizing the importance of the ocean's role in global climate change, IOC and SCOR formed the Committee on Climate Change and the Ocean (CCCCO), with Revelle as its first chairman. In the early 1990s, the international implementation of the Joint Global Ocean Flux Study (JGOFS) resulted from a SCOR activity. The 1992 United Nations Conference on Environment and Development in Rio de Janeiro, Brazil, named IOC as the UN focal point to carry out analysis, assessments and systematic observation of the role of ocean as a carbon sink within the framework of the Action Plan for Global Sustainable Development.

The SCOR-IOC Advisory Panel on Ocean Carbon Dioxide focuses on key issues that are not routinely handled by individual projects, such as how to coordinate carbon-observing programs to eliminate gaps and duplication in activities, and how to standardize ocean carbon measurement techniques and data formats, and provide reliable reference standards. This panel advises global carbon research and monitoring programs (such as the Global Ocean Observing System and the Global Carbon Project) on observations, data management, and modelling needed to understand the ocean component of the global carbon cycle, and to provide an international forum for initiatives to promote high-quality observations of the ocean carbon cycle. As instructed by the IOC Member States, the panel also maintains an

introductory "watching brief" on ocean carbon sequestration (see <http://ioc.unesco.org/iocweb/co2panel>).

## **ABOUT THIS BOOK**

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We hope you will find this book to be helpful, both as a reference during the symposium and afterward. The abstracts for the talks by Invited Speakers are arranged alphabetically by first author. Poster abstracts are arranged alphabetically by first author within each Topic.

## **FACILITIES AT UNESCO**

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The UNESCO building contains many useful facilities for meeting participants:

- Automatic banking machine - on the ground floor down a small corridor on the right as you walk from the main entrance of the UNESCO building towards the conference rooms.
- Bank with exchange facilities - first floor, main building
- Travel agency - first floor, main building
- Cafeteria, a coffee bar with sandwiches and light snacks, and a formal restaurant - 7<sup>th</sup> floor, main building
- Coffee bar with sandwiches, light snacks, coffee and other drinks on the lower level (-1). Look for the "Bar des Conférences".
- You may also find cybercafés at the following nearby addresses:

***Planet-Cyber café***

173 rue de Vaugirard  
Tel: 01 45 67 71 14  
10:30am – 8:00pm 6 days a week

***Cyber'Act***

32 rue des Volontaires  
Tel: 01 53 69 10 60

***skool@rena region***

199 Rue de Vaugirard  
Tel: 01 44 49 02 03  
24/7 closed Sunday 10:00-12:00

***Cyberbase***

215 rue de Vaugirard  
Tel 01 40 56 06 27

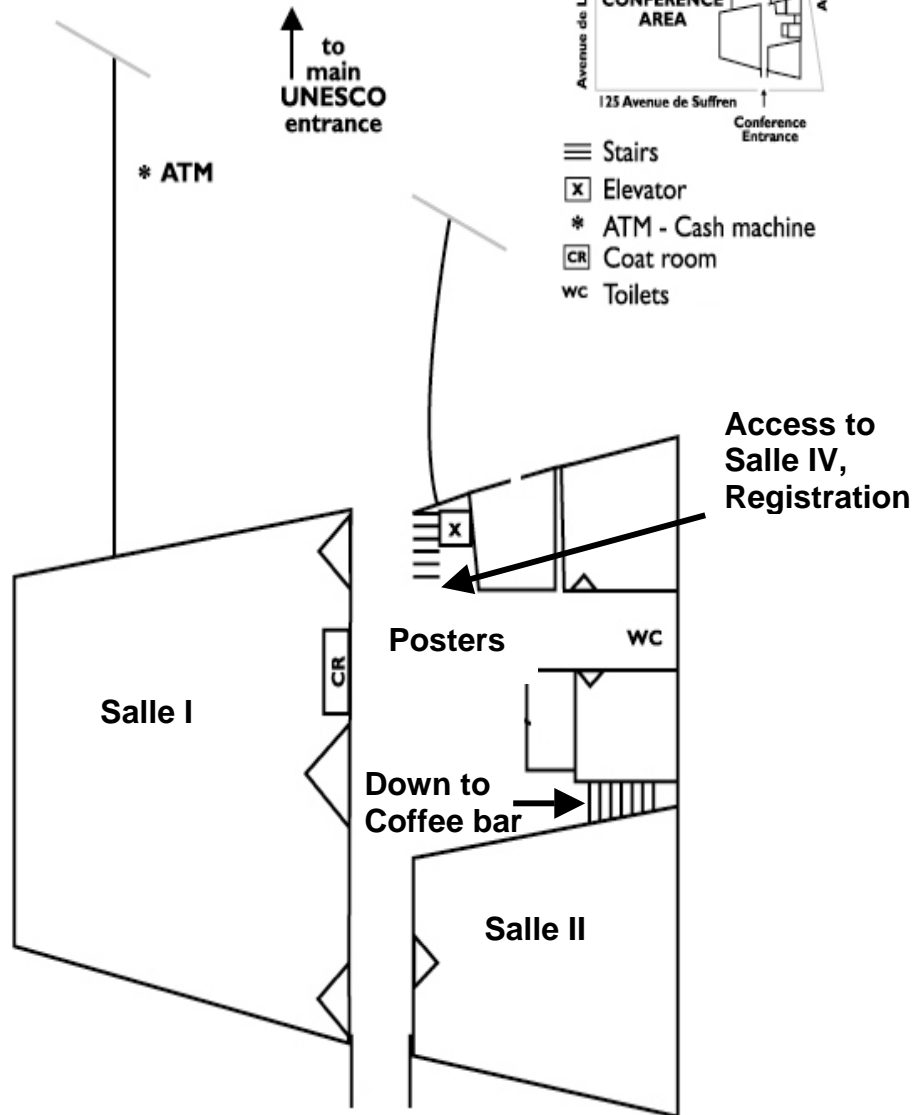
***9c.com***

83-85 rue de Javel  
Tel : 01 56 77 14 00

***Naninet CyberCafé***

43 rue Dutot  
Tel 01 45 66 55 00

# LEVEL 0 (GROUND FLOOR)



- ≡ Stairs
- ⊗ Elevator
- \* ATM - Cash machine
- CR Coat room
- WC Toilets

125 Avenue de Suffren

## **PROGRAMME SUMMARY**

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The symposium has three components:

- Plenary presentations from leading scientists to address issues of biological and chemical effects in the ocean of increasing atmospheric CO<sub>2</sub> concentrations.
- Posters presented by participants at the meeting.
- Discussion sessions to identify priority research topics.

	<b>Monday, 10 May</b>	<b>Tuesday, 11 May</b>	<b>Wednesday, 12 May</b>
7:30	Registration and Poster Set-up		
8:00			
8:30			
9:00	Opening and Welcome	Short- and long-term effects of CO <sub>2</sub> enrichment and surface fertilization on organisms and ecosystems	Discussion Session
9:30	Overview		
10:00			
10:30			
11:00	Break	Break	Break
11:30	Effects of CO <sub>2</sub> Enrichment on Ocean Chemistry	Effects (cont.)	Discussion Session (cont.)
12:00			
12:30	Lunch	Lunch	Lunch
13:00			
13:30			
14:00	Overview of Ocean Carbon Sequestration Strategies	Effects and effectiveness of sequestration techniques: Observational/experimental results	Reports from Discussion Sessions and General Discussion
14:30			
15:00	Discussion Session	Effects and effectiveness of sequestration techniques: Modelling results	
15:30			
16:00	Poster Session with Refreshments	Break	Break
16:30		Modelling Results (cont.)	Closing Summaries
17:00			
17:30			
18:00			



## DETAILED PROGRAMME

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### Notes for Participants

**Talks:** Invited speakers will be expected to adhere to the allocated times for their talks. The chairs of the plenary sessions will be strict about the timing, in order to keep the conference running smoothly.

**Posters:** All poster authors are expected to be present at their poster during the poster session on Monday (16:00-18:00). Posters may also be viewed during all coffee and lunch breaks. Supplies will be provided for mounting the posters.

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## MONDAY, 10 MAY

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9:00 - 9:30

### *Opening and Welcome:*

**Patricio Bernal**, Assistant Director-General UNESCO, Executive Secretary, IOC

**Laurent Labeyrie**, Laboratoire des Sciences du Climat et de l'Environnement, and Vice-President of SCOR

**Ralph Cicerone**, Chancellor, University of California - Irvine, Chair of the International Planning Committee

### *Plenary Session, Overview – Ralph Cicerone, Chair*

9:30 – 10:00

What would be the impacts of climate change assuming no/some/much emissions control and sequestration? - **Martin Parry**, Hadley Centre, UK Met Office

10:00-10:30

Projections of atmospheric CO<sub>2</sub> increases from pre-industrial levels to 2100 and economic implications – **James A. Edmonds**, Joint Global Change Research Institute, College Park, Maryland, USA

10:30 - 11:00

Physical / climate drivers of the ocean in the future – **Laurent Bopp**, LSCE, Gif-sur-Yvette, France

11:00-11:30

**Break**

*Plenary Session, Effects of CO<sub>2</sub> enrichment on ocean chemistry – Peter Liss, Chair*

11:30 - 12:00

Long-term lifetime of fossil fuel CO<sub>2</sub> and its potential effect on the ocean methane hydrate reservoir - **David Archer**, University of Chicago

12:00 - 12:30

Paleo-perspective on ocean pH and carbon cycle - **Edward Boyle**, Massachusetts Institute of Technology

12:30 - 14:00

**Lunch Break**

*Plenary Session, Overview of Ocean Carbon Sequestration Strategies - Peter Haugan, Chair*

14:00 - 14:30

Surface Ocean Fertilization Overview - **Andrew Watson**, University of East Anglia

14:30 - 15:00

The essential science for evaluating direct injection and the emerging high-CO<sub>2</sub> ocean: Designing the next generation of ocean CO<sub>2</sub> experiments – **Peter Brewer**, Monterey Bay Aquarium Research Institute

15:00 - 16:00

**Discussion Session: Identification of Research and Observation Priorities and Approaches - opening discussions. Chris Sabine, Chair**

16:00 - 18:00

**Poster Session** with refreshments

## TUESDAY, 11 MAY

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*Plenary Session, Short and long-term effects of CO<sub>2</sub> enrichment and surface fertilization on organisms and ecosystems – Jean-Pierre Gattuso, Chair*

9:00 - 9:20

Effects of CO<sub>2</sub> on marine animals: Time scales, processes, and limits of adaptation - **Hans-Otto Poertner**, Alfred Wegener Institute for Polar and Marine Research

9:20 - 9:40

Phytoplankton in a high-CO<sub>2</sub> world: Biological responses and their biogeochemical implications - **Ulf Riebesell**, University of Kiel

9:40 - 10:00

Chemical and biological effects on corals in a high-CO<sub>2</sub> world - **Ove Hoegh-Guldberg**, University of Queensland

10:00 - 10:20

Impacts on ocean life in a high-CO<sub>2</sub> world - **Yoshihisa Shirayama**, Kyoto University

10:20 - 10:40

Chemical and biological effects on mesopelagic organisms and communities in a high-CO<sub>2</sub> world - **Louis Legendre**, Laboratoire d'Océanographie de Villefranche

10:40 - 11:00

Chemical and biological effects on fishes in a high-CO<sub>2</sub> world - **Atsushi Ishimatsu**, Nagasaki University

11:00 - 11:30

*Break*

11:30 - 11:50

Ecological effects of deep-ocean CO<sub>2</sub> enrichment: Insights from natural high-CO<sub>2</sub> habitats – **Eric Vetter**, University of Hawai'i

11:50 - 12:10

The ecology of iron-enhanced ocean productivity – **Michael Landry**, Scripps Institution of Oceanography

12:10 - 12:30

Question and Answer Period / Open Discussion

12:30 - 14:00

*Lunch Break*

***Plenary Session, Effects and effectiveness of carbon sequestration techniques: Observational/ Experimental Results – Arne Körtzinger, Chair***

14:00 - 14:30

Synthesis of in situ iron-enrichment experiments - **Hein de Baar**, Royal Netherlands Institute for Sea Research

14:30 - 15:00

Physical and chemical processes affecting release of CO<sub>2</sub> at the seafloor – **Peter Haugan**, University of Bergen

15:00 - 15:30

Biological effects of deep-sea organisms to direct CO<sub>2</sub> injection – **James P. Barry**, Monterey Bay Aquarium Research Institute

***Plenary Session, Effects and effectiveness of carbon sequestration techniques:  
Modelling Results – Jim Orr, Chair***

15:30 - 15:50

Assessing the efficiency of iron fertilization on atmospheric CO<sub>2</sub> using an intermediate complexity ecosystem model of the global ocean – **Olivier Aumont**, LODyC/IPSL/UPMC, Paris, France

15:50 - 16:10

Modelling of dispersion from direct injection in the water column - **Baixin Chen**, National Inst. of Advanced Industrial Science and Technology, Japan

16:10 - 16:40

*Break*

16:40 - 17:00

Glacial-interglacial transitions as analogs for our high-CO<sub>2</sub> future - **Robbie Toggweiler**, Geophysical Fluid Dynamics Laboratory, U.S. National Oceanic and Atmospheric Administration

17:00 - 17:20

Global modelling of the effects of Fe limitation on the natural ocean carbon cycle - **Anand Gnanadesikan**, Geophysical Fluid Dynamics Laboratory, U.S. National Oceanic and Atmospheric Administration

17:20 - 17:40

Global model predictions of ocean chemistry changes for scenarios of atmospheric CO<sub>2</sub> emissions, atmospheric CO<sub>2</sub> stabilization, and ocean CO<sub>2</sub> injection - **Ken Caldeira**, Lawrence Livermore National Laboratory, U.S. Department of Energy

17:40 - 18:00

Question and Answer Period / Open Discussion

## **WEDNESDAY, 12 MAY**

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9:00 - 11:00

***Discussion Session: Identification of Research and Observation Priorities and Approaches - conclusions and drafting. Chris Sabine, Chair***

11:00 - 11:30

*Break*

11:30 - 12:30

Discussion Session, Continued

12:30 - 14:00

*Lunch Break*

14:00 - 16:00

*Report from Discussion Session and General Discussions – Rik Wanninkhof, Chair*

16:00 - 16:30

*Break*

*Closing Summaries – Ralph Cicerone, Chair*

16:30 - 16:50

Summary of implications of the high-CO<sub>2</sub> world for ocean chemistry and how the research community could respond - **Cindy Lee**, State University of New York, Stony Brook

16:50 - 17:10

Summary of implications of the high-CO<sub>2</sub> world for ocean biology and how the research community could respond - **Victor Smetacek**, Alfred Wegener Institute for Polar and Marine Research

17:10 - 17:30

**Ralph Cicerone**, Planning Committee Chair

## INVITED SPEAKERS' ABSTRACTS

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### **Long-term lifetime of fossil fuel CO<sub>2</sub> and its potential effect on the ocean methane hydrate reservoir**

**David Archer**

5712 S. Harper, Chicago, IL 60637, USA

E-mail: d-archer@uchicago

I will assess the long-term atmospheric lifetime of anthropogenic CO<sub>2</sub>, and its potential impact on the stability of the methane clathrate reservoir in the oceans. The fate of fossil-fuel CO<sub>2</sub> is predicted using an ocean circulation / carbon cycle model coupled at each grid point to a model of CaCO<sub>3</sub> dissolution on the sea floor. Approximately ~30% of carbon release to the biosphere will be in the atmosphere after 1000 years (equilibrium with ocean waters), and 10% after 10 kyr (equilibrium with the ocean CaCO<sub>3</sub> cycle). Our assessment of clathrate stability in the face of anthropogenic warming is based on a mechanistic model of the clathrate distribution, driven by predicted anthropogenic warming. Because the temperature impact of anthropogenic carbon decays with time, the magnitude of the clathrate response depends on how quickly it responds, and what fraction of the released carbon escapes the sediment column. Depending on the time-dependence of melting, projected future carbon emissions could easily destabilize the bulk of the clathrate reservoir.

### **Assessing the efficiency of iron fertilization on atmospheric CO<sub>2</sub> using an intermediate complexity ecosystem model of the global ocean**

**Olivier Aumont** and Laurent Bopp

LODyC/IPSL/UPMC, T45-E4 4 Place Jussieu, 75252 Paris cedex 05, France

E-mail: Olivier.Aumont@lodyc.jussieu.fr

Large areas of the ocean, mostly the Subarctic North Pacific, the eastern equatorial Pacific and the Southern Ocean, have been demonstrated to be largely iron limited, in particular by an increasing number of in-situ iron fertilization experiments. Following this finding, the idea of artificially fertilizing the ocean with iron has emerged as a means to mitigate the increase of atmospheric CO<sub>2</sub>. The impact of such fertilization has been examined in the past with very simple biogeochemical models based on the nutrient restoring approach. Here, we used, in a global ocean circulation model, an intermediate complexity ecosystem model, PISCES, which explicitly includes co-limitations by iron, silicate and nitrate. In a first step, patchy iron additions have been performed at various locations of the three main iron-limited regions to mimic the small-scale in-situ fertilization experiments. The objectives were to investigate the model behavior but also, the representativity of the sites selected for these in-situ iron additions. Except in the subarctic Pacific, the model broadly reproduces the main observed features of the biological response to the supply of iron. The failure in the subarctic Pacific is explained by deficiencies in the ocean dynamics leading to a co-limitation by iron but also by the two other limiting nutrients. In the Southern Ocean, the magnitude and the timing of the response display large variations between the

different sites. The major controlling factors are the background iron and silicate concentrations, the physical environment and the timing relative to the growing season. In the equatorial Pacific, these variations are less pronounced, with a maximum response near the Galapagos Island. In a second step, iron fertilization has been performed over the global ocean for fifty years from now using IPCC scenarios for carbon emissions in order to assess its maximum impact on atmospheric CO<sub>2</sub>. The model simulates a rather modest efficiency for this mitigation means. First, the increase in export production induced in the iron-limited regions is balanced by a significant extension of the oligotrophic regions. Second, relieving iron limitation does not necessarily lead to a complete utilization of the available macronutrients, as other limiting factors, like light or grazing come into play. Third, a significant part of the sequestered carbon is remineralized back in the upper ocean and thus is not buried for long time periods.

### **Synthesis of *in-situ* iron enrichment experiments**

**Hein de Baar**, Phil Boyd, Ken Buesseler, Dorothee Bakker, Yann Bozec, Marie Boye, Kenneth Coale, Peter Croot, Patrick Laan, Christiane Lancelot, Maurice Levasseur, Jun Nishioka, Yukihiro Nojiri, Tim van Oijen, Sigenobu Takeda, Klaas Timmermans, Atsuhi Tsuda, Marcel Veldhuis; and co-workers (names in alphabetical order)

Hein de Baar, Royal Netherlands Institute for Sea Research  
P.O. Box 59, 1790 AB Den Burg, The Netherlands  
E-mail: [debaar@nioz.nl](mailto:debaar@nioz.nl)

The initial findings (1987-1992) of strong phytoplankton community responses to iron enrichments in bottles and in natural iron-replete waters of the subArctic Pacific, equatorial Pacific and Antarctic Oceans, have led to a suite of exciting *in situ* Fe enrichment experiments, where simultaneous SF<sub>6</sub> labeling allowed better mapping and tracking of a fertilized patch. Among the wide variety of objectives and observations, here only the impact on phytoplankton, CO<sub>2</sub> and major nutrients is chosen as a modest first start for synthesis.

In the equatorial Pacific IRONEX-1 (1993) did show initial impact but after 4 days was subducted. However Ironex-2 (1995) did lead to a major increase of Chlorophyll *a* and significant removal of both CO<sub>2</sub> and major nutrients. Within the Southern Ocean SOIREE (1999), CARUSO/EISENEX (2000) and two simultaneous SOFEX (2002) fertilizations all led to significant increases of Chlorophyll *a* and removals of dissolved CO<sub>2</sub> and nutrients. Yet except for virtual complete silicate utilization in the northern SOFEX site, not all major nutrient resources were exhausted, this in contrast to parallel shipboard incubations under natural or simulated light conditions. Two fertilizations SEEDS (2001) and SERIES (2002) in the western and eastern subArctic Pacific respectively, both led to intense blooms, uptake of CO<sub>2</sub> and (virtually complete) removal of major nutrients.

Photosynthesis requires adequate light. Somewhat IRONically, the one apparent hypothesis from comparison of these 8 iron experiments is that the depth of the Wind Mixed Layer (WML) in defining light climate is the primary limiting factor. This is now being tested with a generic plankton ecosystem simulation model. The

experiments of the Southern Ocean appear to have suffered most from very deep WML, where self-shading in the bloom may also have played a role. In contrast this light limitation has largely been alleviated due to favorable WML conditions during IRONEX-2 and SEEDS and SERIES, but of course light became limiting after subduction of the IRONEX-1 patch. Thus the Southern Ocean experiments seem to have been strongly light-limited, as opposed to the equatorial Pacific (IRONEX-2) and the subArctic Pacific (SEEDS, SERIES). During austral summer (December-January) in the Southern Ocean incident light is optimal and average wind velocities are somewhat less: a shallow WML is common and has been observed to exist in specific regions. The recent EIFEX (January-March 2004) experiment may or may not have encountered such more favorable light conditions.

A second observation is the shift-up to larger size classes of diatoms, except for the southern SOFEX site where all compartments of the plankton community appeared to be responding. This stimulus of large diatoms is consistent with ALL preceding bottle incubations and natural Fe-replete regions, as well as with individual diatom species in natural HNLC seawater experiments in the laboratory. The variability of available Fe within a patch likely has affected the success of one or another size class of diatoms.

Various approaches for assessing net sequestration of notably carbon into deeper waters will be compared. Moreover patch dilution, and artefacts versus bottle incubations and unperturbed natural systems will be discussed. Synthesis of the recent 9 experiments is advisable in order to design the next generation of experimental oceanography. For example insights in chemistry of added Fe versus natural seawater are already leading to new initiatives in natural laboratories (FeCYCLE 2003; BICEP 2004 at Crozet; KEOPS 2005 at Kerguelen) of iron-ecosystem interactions. The new *in situ* ocean Fe enrichment experiments likely will require concerted multi-ship strategy as pioneered admirably in SOFEX.

### **Biological responses of deep-sea organisms to direct CO<sub>2</sub> injection**

**James P. Barry**, Kurt R. Buck, Linda Kuhnz, Patrick J. Whaling, Chris Lovera, Jeff C. Drazen, Mario N. Tamburri, Brad A. Seibel, Edward. T. Peltzer III, Peter Walz, and Peter G. Brewer

Monterey Bay Aquarium Research Institute  
7700 Sandholdt Road, Moss Landing, CA 95039 USA

E-mail: Barry@mbari.org

Purposeful injection of CO<sub>2</sub> into the deep sea is one of several carbon management options that may be employed to mitigate the accelerating rise in atmospheric CO<sub>2</sub> levels. Although recent models indicate that direct ocean CO<sub>2</sub> injection is a feasible option for carbon management, our understanding of the effects of a large-scale CO<sub>2</sub> injection program on deep-sea ecosystems remains poor. Deep-sea animals are generally intolerant of environmental variability, and may be vulnerable to changes in ocean chemistry caused by CO<sub>2</sub> injection. The addition of gT levels of CO<sub>2</sub> into the deep sea will elevate pCO<sub>2</sub> and reduce ocean pH from ~3+ pH units near release sites, to perhaps -0.1 to -0.3 units over large areas of the deep ocean.



We evaluated the response of various deep-sea animals to deep-sea CO<sub>2</sub> injection during in situ experiments in which animals were exposed to the dissolution plume emanating from pools of liquid CO<sub>2</sub> released onto the seafloor. Study animals included infaunal meiofauna, macrofaunal crustaceans, megafaunal invertebrates, and fishes, which were held in cages near CO<sub>2</sub> pools. During these ~month-long experiments, animals held in cages or inhabiting the sediment, were exposed intermittently to CO<sub>2</sub>-rich, low pH seawater drifting downstream from CO<sub>2</sub> pools. Rates of survival varied among taxa, but were generally low near CO<sub>2</sub> pools, where pH was reduced by up to 1.5 pH units during short periods when tidal flow carried the CO<sub>2</sub> plume directly over the animals. Mortality of 80% and greater was common for meiofauna, macrofaunal amphipods, and deep-sea echinoderms. Deep-sea eelpout fishes, however, exhibited high rates of survival, even near CO<sub>2</sub> pools. Mortality rates of all organisms were lower, though still significant, at distances of 10 to 20 m from CO<sub>2</sub> pools, where pH was reduced by ~0.2 units episodically. The plume was nearly undetectable 50 m from CO<sub>2</sub> pools, where animals were considered to be unaffected by the plume. Sublethal impacts of CO<sub>2</sub> exposure were not detected. Results from these experiments suggest that the sensitivity of deep-sea benthic organisms to elevated CO<sub>2</sub> levels is high. Due to the rotary character of near-bottom currents, however, exposure to the dissolution plume from CO<sub>2</sub> pools was intermittent, limiting our interpretation of potential threshold concentrations for CO<sub>2</sub> tolerance by deep-sea animals.

While the injection of CO<sub>2</sub> into deep-ocean environments is likely harmful to deep-sea ecosystems, the integrated effects of ocean sequestration must be considered globally. Any anticipated impacts on deep-ocean ecosystems must be assessed relative to the role of ocean CO<sub>2</sub> sequestration in mitigating the effects of both unabated greenhouse warming and the chronic acidification of shallow ocean environments.

## **Physical / chemical drivers of the ocean in the future**

### **Laurent Bopp**

LSCE/IPSL, Gif sur Yvette, France

E-mail [bopp@lsce.saclay.cea.fr](mailto:bopp@lsce.saclay.cea.fr)

The physico-chemical habitat of the ocean and its interaction with marine biota is fundamental (1) in determining marine biogeochemical responses to climate change and (2) in estimating the potential feedbacks on climate that may arise from those responses. Using results from climate and marine biogeochemical models, we review some of the major physical and chemical changes that the ocean will undertake in the coming decades and illustrate how these changes may affect marine biogeochemistry and drive feedbacks on climate. We identify three classes of physico-chemical changes:

(1) Most of carbon dioxide released in the atmosphere from fossil fuel burning will be absorbed by the ocean and eventually result in large marine pH changes. Making the ocean more acidic, these changes have the potential to affect coral reef, calcareous plankton and other organisms with shells containing calcium carbonate; a decrease of

calcium carbonate production in the ocean would act as a negative feedback on rising atmospheric CO<sub>2</sub>.

(2) Climate models' simulations of global warming predict widespread oceanic temperature increases and large changes in oceanic stratification, circulation and convective overturning. Those changes have the potential to affect all marine biogeochemical cycles but also marine productivity and the ecosystem structure. Enhanced stratification for example is expected to decrease the amount of anthropogenic carbon taken up by the ocean; to decrease the dissolved oxygen content of subsurface waters; and to decrease nutrient supply to surface waters everywhere, but to increase light supply through increasing the growing season length at high latitudes. Overall, recent models suggest that changes in the physical properties of the ocean with global warming would act as a positive feedback on rising atmospheric CO<sub>2</sub>.

(3) Recent studies have shown that oceanic nutrient supply from atmospheric deposition may respond to global warming by a decrease as large as -60% at the end of this century. This effect, although largely uncertain, has the potential to affect marine productivity and the ecosystem structure through a decrease of the iron content of surface waters. Leading to a reduction in marine productivity, this effect would act as a positive feedback on rising atmospheric CO<sub>2</sub>.

### **Paleo-perspective on ocean pH and the carbon cycle**

#### **Edward A. Boyle**

Department of Earth, Atmospheric and Planetary Sciences, E34-258  
Massachusetts Institute of Technology, Cambridge MA USA 02139  
eaboyle@MIT.EDU

We can directly observe atmospheric CO<sub>2</sub> variability during the past 400,000 years, but we may not be able to explain this variability. We can't directly observe CO<sub>2</sub> variability for older times, but we have several models that can explain this variability.

Ice core observations of atmospheric CO<sub>2</sub> variability from 190 to 280 ppmV between glacial and peak interglacial times are the most robust paleoclimatic knowledge that we have about the past carbon cycle. No matter what the cause of this change it would require an increase of about 0.13 pH unit in tropical and subtropical surface waters. Although we can account quite well for some factors that influence glacial/interglacial CO<sub>2</sub> change (glacial reductions in ocean temperature and continental biomass, the increased salinity of the ocean, and the carbonate ion response), these factors do not explain more than about half of the amplitude of the observed CO<sub>2</sub> change unless extreme scenarios are allowed. Interestingly, the pH and carbonate ion responses to some of these factors are significantly different. If we reduce p CO<sub>2</sub> from 280 to 190 ppmV through any combination of dissolved CO<sub>2</sub>, alkalinity and temperature changes, the pH response is always the same. But CO<sub>2</sub> and alkalinity changes that lower p CO<sub>2</sub> by the same amount increase the carbonate ion concentration by 60-95 micromoles/kg, whereas a temperature change that lowers p CO<sub>2</sub> by the same amount REDUCES the carbonate ion concentration by 8 micromoles/kg. I will review the

status of the boron isotope paleo-pH proxy and various proposed paleo-carbonate ion proxies to see if we can utilize this difference to delimit the causes of lowered glacial CO<sub>2</sub>.

On the longer time scale of millions to hundred millions of years, we can't observe CO<sub>2</sub> directly, although several proxies have been proposed to stand in for direct CO<sub>2</sub> measurements and numerous models exist to explain why CO<sub>2</sub> concentrations have been higher in the past. A recently published conceptual model by Edmond and Huh (2003) may provide the most reasonable explanation for geologically low CO<sub>2</sub> in the present era.

### **The essential science for evaluating direct injection and the emerging high-CO<sub>2</sub> ocean: Designing the next generation of ocean CO<sub>2</sub> experiments**

**Peter G. Brewer**, William Kirkwood, and James Barry  
Monterey Bay Aquarium Research Institute, Moss Landing, CA 95039, USA  
E-mail: [brpe@mbari.org](mailto:brpe@mbari.org)

By the end of the 20<sup>th</sup> Century any concerns about the ability to recover the signal of fossil fuel CO<sub>2</sub> in sea water had vanished; fossil fuel CO<sub>2</sub> is now a major ion of sea water, and it is accumulating in the upper ocean at a rate of ~25 million tons per day. The ocean has now absorbed some 400 billion tons of fossil fuel CO<sub>2</sub>, ~ 50% of this is stored in the upper 250m, and biogeochemical impacts, which will inevitably be imprinted on the associated climate change, are beginning to be questioned. Simple calculations show that by mid-21<sup>st</sup> Century the surface ocean could experience a ~ 0.3 pH unit change, with further significant decreases to follow. Is this a serious problem, and what should ocean scientists do to investigate this?

Direct injection of CO<sub>2</sub> into the deep ocean has been considered as one strategy to moderate both climate change and the accumulation in the upper ocean, and the first small-scale experiments have been carried out. This has raised fears of biological impacts from lowering deep ocean pH; yet deep injection of even 1% (250,000 tons per day) of the present day surface ocean invasion rate would require such a large investment that it is highly unlikely that this will take place in the near future. Even then, 99% of our environmental concern should logically be directed at the extraordinary upper ocean changes now occurring. The 20<sup>th</sup> Century approach of long survey cruises and time-series stations will not alone be effective as a way to address this issue and a new attack is called for.

We describe here the potential science and technology of carrying out novel actively controlled CO<sub>2</sub> perturbation experiments in the ocean in much the same way that ecosystems are exposed to elevated CO<sub>2</sub> levels on land through the Free Air CO<sub>2</sub> Enrichment (FACE) program.

This could involve creation of a ring of pipes and sensors (pH, velocity etc), cabled to shore for control, and diffusing either small volumes of CO<sub>2</sub> or acid on the upstream side, so that a relatively constant perturbation of the CO<sub>2</sub> system is maintained within the experimental area for long periods of time. For shallow waters, such as coral reef systems, this may be installed and maintained by divers. For deeper systems new,

sophisticated ROV techniques would be required. Fundamental challenges of system control and observation are now being actively investigated.

### **Global model predictions of ocean chemistry changes for scenarios of atmospheric CO<sub>2</sub> emissions, atmospheric CO<sub>2</sub> stabilization, and ocean CO<sub>2</sub> injection**

**Ken Caldeira**<sup>1</sup>, James C. Orr<sup>2</sup>, and Michael E. Wickett<sup>1</sup>

<sup>1</sup>Energy and Environment Directorate, LLNL, 7000 East Ave, L-103, Livermore CA 94550 USA

<sup>2</sup>LSCE, CEA Saclay, Bat. 709, L'Orme, F-91191 Gif-sur-Yvette Cedex, France  
kenc@llnl.gov

We present the results of calculations of ocean chemistry changes based on ocean general circulation model results for scenarios of (1) release of CO<sub>2</sub> to the atmosphere, (2) stabilization of atmospheric CO<sub>2</sub>, and (3) release of CO<sub>2</sub> to the ocean interior.

Ocean Carbon-cycle Model Intercomparison Project (OCMIP) results indicate model-to-model differences in predicted ocean chemistry changes for a range of scenarios of atmospheric CO<sub>2</sub> release, atmospheric CO<sub>2</sub> stabilization, and deep-ocean CO<sub>2</sub> injection. Simulations made with the LLNL ocean model indicate how ocean chemistry changes scale with emissions rate, stabilization scenarios, and rates of deep ocean injection.

We find that for all scenarios considered surface ocean chemistry largely tracks atmospheric CO<sub>2</sub> content, and that surface ocean chemistry changes can be approximated assuming equilibrium with atmospheric CO<sub>2</sub>. For atmospheric CO<sub>2</sub> release and stabilization scenarios, excess carbon accumulates first in the relatively well-ventilated isopycnal layers of the upper thermocline, with deeper penetration initially confined to the North Atlantic and Southern oceans. In contrast, CO<sub>2</sub> injected into the ocean interior is retained in the poorly ventilated isopycnal layers of the deep ocean, but is lost to the atmosphere from the well-ventilated layers of the upper thermocline.

Depending on size estimate of ultimate fossil fuel resource (which could include CO<sub>2</sub> from methane hydrates, etc.), unrestrained release of fossil fuel CO<sub>2</sub> has the potential to produce surface ocean conditions that are undersaturated with respect to calcite and aragonite. Release of CO<sub>2</sub> on this scale to the atmosphere, or directly to the ocean, has the potential to produce ocean chemistry changes outside the range estimated for the past several hundred million years from paleo-CO<sub>2</sub> proxies and carbonate-silicate models of the carbon cycle on tectonic time scales. Changes in ocean chemistry of this magnitude have been shown to be biologically significant.

## Modelling of dispersion from direct injection in the water column

### Baixin Chen

National Institute of Advanced Industrial Science and technology, Japan  
Thermal Engineering Research Group, AIST  
Tsukuba East, Tsukuba 305-8564, Japan  
E-mail: b.chen@aist.go.jp

In this paper, we attempt to predict the double-plume formation and dispersion dynamics from direct injection of CO<sub>2</sub> into ocean water at middle depth through a three-dimensional two-fluid numerical model. The model consists of a CO<sub>2</sub> droplet sub-model and a small-scale turbulent ocean sub-model, both of which are subjected to the examination of field observation data.

We report here the numerical results on examination of the roles of injection technologies, initial parameters, and ocean environments on characteristics of droplet and CO<sub>2</sub>-enriched seawater plumes, respectively. For the geometric properties of the plumes, our results show that the vertical distances that could be occupied by the plumes were governed dominantly by initial droplet diameter ( $D_0$ ) and then by injection depth ( $H_{inj}$ ). At conditions of injection rates ranging from 0.1kg/s to 1.0kg/s and ocean current speeds from 2.5cm/s to 25cm/s, this vertical distance increased with a rate of approximately 25m/mm (droplet diameter) from 45m when  $D_0=3$ mm to 250m when  $D_0=10$ mm for  $H_{inj}=1000$ m; while decreased from 662m when  $H_{inj}=2000$  to 580m when  $H_{inj}=1200$ m for  $D_0=20$ mm. Horizontally, CO<sub>2</sub> enriched water plume can be dispersed and streaked with the turbulent ocean flow from initial area of 0.45 to  $9.8 \times 10.5$  km<sup>2</sup> in 100 hours.

The concentration distribution characters of CO<sub>2</sub> enriched seawater plume, however, are produced with interplays among ocean turbulent flow, initial parameters, and injection technologies. This concentration distribution character is discussed in terms of a so-called concentration distribution function, which is defined as a ratio of the volume with DCO<sub>2</sub> concentration larger than a given value to the volume of entire plume. As a general rule, ocean current and turbulence enhanced the dilution of the plume, while the larger injection rate and smaller initial droplet would produce a DCO<sub>2</sub> dense plume. Numerical simulations predicted that injection of CO<sub>2</sub> from fixed ports at a rate of 0.6kg/s and  $D_0=8$ mm at 800m to a normal current ocean (the basic case) could create a plume with local pH drop about 1.6 value, but a plume with local pH drop only about 0.8 value to a benthic storm ocean. This small pH drop could be achieved alternatively by decrease of injection rate to 0.1kg/s for the basic case. On the other hand, strong ocean turbulence can counteract the gravity flow due to enhanced concentration of DCO<sub>2</sub>, which leads to the CO<sub>2</sub>-enriched seawater column experienced as a dynamically passive tracer. Finally, it was found for cases of release of CO<sub>2</sub> from a towered pipe that horizontal pipe option is much better than vertical pipe option (with 10 times larger in concentration than that of horizontal option) if the objective is to dilute CO<sub>2</sub>-enriched water column.

We concluded from our numerical studies that we suggest to release large CO<sub>2</sub> droplet from a horizontal pipe towered by a moving ship at depths of about 2000m in order to minimize the influence on marine life.

## **Projections of atmospheric CO<sub>2</sub> increases from pre-industrial levels to 2100 and economic implications**

**James A. Edmonds**, Hugh Pitcher and Steven J. Smith

<sup>1</sup>Joint Global Change Research Institute, 8400 Baltimore Avenue, Suite 201 College Park, MD 20740-2496, USA

E-mail: [jae@pnl.gov](mailto:jae@pnl.gov)

In this paper we consider the prospect for future emissions of CO<sub>2</sub> and other greenhouse related gases including the sources of emissions and factors shaping the scale of primary determinants of future emissions. We review historical emissions. We consider population growth and potential future trends. We further consider economic forces including gross domestic product, fossil fuel resource availability, technology and public policy. Finally, we remark on potential future emissions of other greenhouse related gases and implications for climate change.

## **Global modelling of the effects of Fe limitation on the natural ocean carbon cycle**

**Anand Gnanadesikan**

Geophysical Fluid Dynamics Lab, P.O. Box 308, Princeton NJ 08542, USA

E-mail: [gnana@ceto.princeton.edu](mailto:gnana@ceto.princeton.edu)

Many conceptual models of carbon dioxide sequestration via iron fertilization assume that there is a tight linkage between iron input, productivity, carbon export, and carbon sequestration. In this paper we present a set of box models showing that this linkage is not nearly as tight as might be expected. In particular, the effectiveness of iron fertilization depends sensitively on the details of iron cycling within the global ocean.

## **Physical and chemical processes affecting release of CO<sub>2</sub> at the seafloor**

**Peter M. Haugan**

Geophysical Institute, University of Bergen, Allegaten 70, N-5007 Bergen, Norway

E-mail: [Peter.Haugan@gfi.uib.no](mailto:Peter.Haugan@gfi.uib.no)

CO<sub>2</sub> can be released at the seafloor as gas, liquid, hydrate, solid (dry ice), or dissolved in seawater. It can be purposefully placed at the seafloor or seep through the seafloor from subseabed placement. In order to meaningfully assess the fate of this CO<sub>2</sub> and its biological impact, there is a need to describe and understand some physio-chemical nearfield processes and their interaction with ocean hydrodynamics and turbulence. Basic, but sometimes unexpected, thermodynamic properties such as the increase in seawater density due to dissolution of CO<sub>2</sub> are important.

Early deep-ocean storage concepts envisioned a stable lake of liquid CO<sub>2</sub> overlain by a thin hydrate layer with slow dissolution analogous to natural brine pools. However, exposure to ocean currents such as benthic storms has been shown theoretically, and recently also in deep-sea experiments, to be able tear up the interface by Kelvin-Helmholtz instabilities. The stabilizing effect of the hydrate layer and the seawater

density increase due to dissolution is insufficient to overcome the destabilising effect of current shear. Thus, near local depressions where pure liquid CO<sub>2</sub> is placed, the deep-sea environment may be exposed to dense gravity currents with elevated carbon concentrations and reduced pH.

Seepage of CO<sub>2</sub> from geological subseabed storage may occur in shallow water where pure CO<sub>2</sub> would be in gas phase and thus might be expected to escape rapidly to the atmosphere. However, slow gas seepage, for example, into an isolated depression or non-tidal basin, transition through a hydrate stage, or flow of CO<sub>2</sub>-enriched water from below the seafloor, could create a layer with high concentration of dissolved CO<sub>2</sub> even in shallow water. Turbulent mixing and dilution of a CO<sub>2</sub>-enriched bottom boundary layer is then a key fluid dynamical problem that needs to be understood in order to assess CO<sub>2</sub> release at the seafloor. In addition the complex physics and chemistry of hydrate formation and dissolution remains an experimental and theoretical challenge.

Presently, a two-layer CO<sub>2</sub>-seawater model is used where the effects of hydrate are parameterized via dissolution and interfacial tension. Scenario calculations can be made, but deep-sea experiments will be required to improve confidence in model estimates.

## **Chemical and biological effects on corals in a high-CO<sub>2</sub> world**

### **Ove Hoegh-Guldberg**

Centre for Marine Studies, University of Queensland, St Lucia, 4067, QLD, Australia  
E-mail: oveh@uq.edu.au

The consequences of a changing atmosphere for coral reefs are serious and are already occurring. With periods of abnormally warm seas and carbon dioxide concentrations above any seen for the last 400,000 years, corals are facing conditions that greatly exceed the environmental envelope to which they are adapted. Evidence that this is occurring is seen in the increasing frequency and severity of mass bleaching events, in which corals lose their brown symbionts and turn white. Increasingly, these events are resulting in large-scale mortalities, a consequence of longer and more intense warming during the summer months. The impact of increasing sea temperatures is being compounded by the changing aragonite saturation state of seawater ( $\Omega$ -arag). Oceanic  $\Omega$ -arag will continue to decrease over the next 50 years as CO<sub>2</sub> builds up the atmosphere. Decreased  $\Omega$ -arag directly reduces the calcifying ability of organisms such as corals, eventually making their skeletons fragile. While corals and coral reefs are unlikely to undergo complete extinction in geological time, the prognosis for reefs and the people that depend on them is not bright in the shorter term (tens to hundreds of years). Analysis using projected sea temperatures and the current sensitivity of corals to elevated sea temperatures indicates that conditions will soon greatly exceed the thermal thresholds of corals and their symbionts, with the consequence that major mortalities will be commonplace by 2030 and thermal stress events will rise above any experienced by corals in the past 50 years if not several thousand years. Given the importance of coral reefs to billion dollar economies and an estimated 100 million people worldwide, action must be taken to reduce these impacts. The first step has to be a

major reduction in greenhouse gas emissions and eventually the rate of global warming. Given the sensitivity of corals to changes in sea temperature, stabilization of the global temperature at no more than 2°C above pre-industrial temperatures must be achieved. Stabilization is critical in itself if re-assortment of corals is to occur from low to high latitudes, and newly arrived thermal genotypes are to flourish in these new locations. The second step has to be to reduce the many other stresses (sedimentation, eutrophication, over-exploitation) that are currently impacting the world's coral reefs. Without reducing these other stresses, the ability of corals and coral reefs to bounce back from climate-driven events over the next 10-100 years will be vastly reduced.

### **Chemical and biological effects on fishes in a high-CO<sub>2</sub> world**

**Atsushi Ishimatsu**, M. Hayashi, K.-S. Lee, T. Kikkawa<sup>1</sup> and J. Kita<sup>2</sup>

Marine Research Institute, Nagasaki University

<sup>1</sup>Central Laboratory, Marine Ecology Research Institute

<sup>2</sup>Research Institute of Innovative Technology for the Earth

E-mail: a-ishima@net.nagasaki-u.ac.jp

Fish gill ventilation is mainly governed by O<sub>2</sub> stimuli because of the far lower solubility of O<sub>2</sub> than CO<sub>2</sub> in water. Thus, fish hyperventilate in terms of CO<sub>2</sub> excretion, resulting in low CO<sub>2</sub> partial pressures (2-4 torr) in fish body as compared with air-breathing animals (for example 40 torr in man). Elevations of ambient CO<sub>2</sub> levels will therefore easily cause inward diffusion of CO<sub>2</sub>, and acidifies body fluid. Although fish have efficient body-fluid buffering mechanisms, acidification of the internal medium will perturb multiple physiological processes, and when CO<sub>2</sub> level is beyond tolerance limits, death ensues.

In earlier studies, toxicity data of nonvolatile acids (HCl, H<sub>2</sub>SO<sub>4</sub> etc.) were used to evaluate toxic effects of CO<sub>2</sub> on marine organisms. When fish eggs and larvae were exposed to seawater acidified either by CO<sub>2</sub> or HCl to the same pH, CO<sub>2</sub> exposure resulted in far higher mortalities than HCl (62-85% and 2-4% at pH 6.2, 97-100% and 1-5% at pH 5.9). Thus, the use of acid data to evaluate CO<sub>2</sub> toxicity is invalid.

Embryos and larvae are often more susceptible to environmental impacts, so effects of CO<sub>2</sub> on fish during these early developmental stages must be carefully studied. We recently studied both short-term and long-term effects of CO<sub>2</sub> on several marine fish during early stages. Test fish (two species with different lifestyle) showed a similar characteristic pattern of CO<sub>2</sub> susceptibilities with development; the egg and juvenile stages were more susceptible while the stages in between were tolerant. Ion transporting mitochondria-rich cells (MR cells) increased in size during CO<sub>2</sub> exposure, suggesting their role for pH regulation. A 150-day exposure to CO<sub>2</sub> (0.4-1.2%) decreased growth of a juvenile marine fish.

The drop of blood pH by CO<sub>2</sub> exposure was nearly completely restored by accumulation of bicarbonate ions. Plasma chloride ions significantly decreased during compensation, again suggesting the involvement of MR cells (the definite site of chloride extrusion in marine fish) in the process. However, death could occur after complete pH restoration. Blood output from the heart immediately decreased in



response to CO<sub>2</sub> exposure. O<sub>2</sub> supply to the tissues declined despite increased blood O<sub>2</sub> concentration. We tentatively conclude that the drop of tissue O<sub>2</sub> supply plays an important role in fish kill mechanisms by high CO<sub>2</sub>.

To evaluate effects of CO<sub>2</sub> sequestration on fish at injection sites, experiments must be done at low temperatures and high pressures using deep-water species.

### **The ecology of iron-enhanced ocean productivity**

**Michael R. Landry**

Scripps Institution of Oceanography, University of California, San Diego, 9500

Gilman Dr., La Jolla, CA 92093-0227

E-mail: mlandry@ucsd.edu

Mesoscale enrichment experiments over the past decade have established that low-level iron addition can substantially enhance the primary productivity of high-nutrient regions representing a large fraction of the ocean's surface area. Whether this iron-stimulated new production can provide, in turn, a globally significant deep-sea sink for rising atmospheric carbon is a matter of some debate. Quite aside from issues of sequestration potential or efficacy, the contemplated scale of commercially envisioned iron fertilization challenges our basic understanding of the ecological dynamics of upper ocean ecosystems. How would open-ocean systems respond to chronically altered states of nutrient flux and productivity? How might these impact the life histories of key organisms, community diversity, resiliency, fisheries yield, or other indices of system health or human concern? While powerful in many respects, the small, short-term perturbation studies to date have not captured the relevant scales for assessing true ecological responses and community adaptations. Neither can we hope to find answers in the current biologically simplistic state of marine ecosystem modeling. The present talk considers what we do know about the early stages of system response to iron fertilization and what we need to know to put the consequences of large-scale manipulations of this type into long-term ecological context.

### **Chemical and biological effects on mesopelagic organisms and communities in a high-CO<sub>2</sub> world**

**Louis Legendre**<sup>1</sup> and Richard B. Rivkin<sup>2</sup>

<sup>1</sup>Villefranche Oceanography Laboratory, BP 28, 06234 Villefranche-sur-Mer Cedex, France

<sup>2</sup>Ocean Sciences Centre, Memorial University of Newfoundland, St. John's, NF A1C 5S7, Canada

E-mail: legendre@obs-vlfr.fr

Marine food webs influence climate by channelling carbon into the ocean's interior (i.e., sequestration). Because most of the organic matter exported from the euphotic zone is remineralised within the upper 1000 m of the water column (i.e., the mesopelagic layer), and the resulting CO<sub>2</sub> would potentially come back to the atmosphere on decadal time scales, the processes within the water column down to the

depth of sequestration, that is, 1000 m, must be considered in ocean-climate models. Because of the increased atmospheric and marine CO<sub>2</sub> concentrations, four main marine environmental factors will likely increase in the coming decades: water temperature; pCO<sub>2</sub>; mechanical energy (storm activity) which, when combined with temperature, will influence rate of nutrient replenishment from below (pycnocline strength) and nutrient loading (pycnocline depth); and aeolian inputs of inorganic macro- and micronutrients (e.g., Fe), and organic substrates (DOM). These changes will influence the structure and dynamics of most plankton groups, for example, taxonomic composition, biomass, production (growth) and respiration. Hence, relevant models must take into account the roles of plankton organisms in determining the biogeochemical fluxes of carbon, in order to predict interactions between climate change and the ocean's biology. We propose that the new class of models should consider the interactions of at least five major functional groups of plankton organisms (phytoplankton, heterotrophic bacteria, microzooplankton, mesozooplankton, and microphagous macrozooplankton), four biogeochemical carbon fluxes (photosynthesis, calcification, respiration, and deep transfer) and three classes of food-web processes that affect organic matter (synthesis, transformation, and remineralisation). We present the framework of a conceptual model that integrates marine planktonic food webs, oceanic biogeochemistry and ocean-climate interactions in the mesopelagic layer, and propose a plan for its implementation in a high-CO<sub>2</sub> world.

### **What would be the impacts of climate change assuming no/some/much emissions control and sequestration?**

#### **Martin Parry**

Hadley Centre, UK Met Office, Fitzroy Road, Exeter EX1 3PB, UK

E-mail: parryml@aol.com; ipccwg2@metoffice.com

This presentation will describe the range of projected effects of climate change for different levels of concentration of atmospheric greenhouse gases. The general measure of effect is 'people at risk', and this risk is measured in terms of vulnerability to hunger, to water shortage, to coastal flooding and to malaria. Unmitigated climate change is estimated to lead, by the 2050s and 2080s, to an additional hundreds of millions of people at risk (in the case of water to thousands of millions). To draw down these levels of risk will require major reductions in concentrations: more than a half of the increase in concentrations due to human activity will need to be avoided to escape the occurrence of intolerable levels of risk.

### **Effects of CO<sub>2</sub> on marine animals: Time scales, processes, and limits of adaptation**

**Hans O. Pörtner**<sup>1</sup>, Martina Langenbuch<sup>1</sup>, and Basile Michaelidis<sup>2</sup>

<sup>1</sup> Alfred-Wegener-Institute, Bremerhaven, Germany

<sup>2</sup>School of Biology, Aristotle University of Thessaloniki, Greece

E-mail: hpoertner@awi-bremerhaven.de

Rising CO<sub>2</sub> levels in the atmosphere and in marine surface waters as well as projected scenarios of CO<sub>2</sub> disposal in the ocean emphasize that CO<sub>2</sub> effects on aquatic organisms, especially animals, need to be investigated to identify sensitive physiological processes. Development of a mechanistic cause and effect understanding is required as well as a quantification of tolerance windows or thresholds relevant for ecosystem functioning. CO<sub>2</sub> elicits an acidosis in body fluids and tissues where it is compensated for to various degrees by bicarbonate accumulation. Only a few organisms like squid are expected to show an acute sensitivity related to acidosis caused by moderate CO<sub>2</sub> increments. The level of sensitivity is likely due to high metabolic rate and an extremely pH-sensitive oxygen transport via their extracellular blood pigment, haemocyanin. However, long-term effects may set in rather early in a wider range of organisms and elicit shifts in ecological equilibria. Such effects not only include a disturbance in calcification. Recent studies of invertebrate fauna pre-adapted to oscillating CO<sub>2</sub> levels in their habitat revealed a depression of metabolic rate caused by a reduction in ion exchange and protein synthesis rates as well as a shift in metabolic equilibria. As seen in mussels hypercapnia caused a slowing of growth, likely related to the reduction in metabolic rate and the concomitant dissolution of shell CaCO<sub>3</sub> as a result of extracellular acidosis. Although such effects may not be detrimental on short to medium time scales, enhanced mortality occurs under long-term moderate hypercapnia with as yet unidentified cause and effect relationships.

On evolutionary time scales extant animal life, especially those life forms displaying high levels of performance, evolved only when atmospheric CO<sub>2</sub> had fallen far below Cambrian levels of 5000 ppm. A detrimental role of elevated aquatic CO<sub>2</sub> levels has been suggested to contribute to later mass extinction events in Earth history. Long-term CO<sub>2</sub> effects as discussed above are apparently in line with this consideration. However, these analyses ignored that elevated CO<sub>2</sub> levels may only have become effective because they were paralleled by concomitant fluctuations in two other factors, temperature and oxygen. In fact, extreme temperature oscillations were discussed to play the key role in mass extinction events in Earth history. Concomitant increments in CO<sub>2</sub> levels and hypoxia would enhance sensitivity to thermal extremes. Similar interactions should be considered in currently discussed scenarios to dispose of anthropogenic CO<sub>2</sub> in the oceans, either directly by injection into the deep ocean or indirectly during iron fertilization and the subsequent export of organic material into deeper waters, where it will enhance the threat of hypoxia due to oxygen demanding degradation.

### **Phytoplankton in a high-CO<sub>2</sub> world: Biological responses and their biogeochemical implications**

**Ulf Riebesell**

Institut für Meereswissenschaften, IFM-GEOMAR, Düsternbrooker Weg 20

24105 Kiel, Germany

E-mail: [uribesell@ifm-geomar.de](mailto:uribesell@ifm-geomar.de)

Rising atmospheric CO<sub>2</sub> and the related changes in seawater carbonate chemistry directly affect the two primary carbon-fixing processes in the ocean, biogenic CaCO<sub>3</sub> precipitation and photosynthetic CO<sub>2</sub> fixation. A doubling in present-day atmospheric

CO<sub>2</sub> concentration is predicted to cause a 20-40% reduction in the CaCO<sub>3</sub> production by the three major calcifying groups, the coccolithophores, foraminifera and corals. With ca. 90% of global CaCO<sub>3</sub> precipitation contributed by planktonic organisms, reduced calcification lowers the vertical transport of calcium carbonate (and hence alkalinity) to the deep sea. This increases the CO<sub>2</sub> storage capacity of the surface ocean, thus comprising a negative feedback to anthropogenic CO<sub>2</sub> increase.

CO<sub>2</sub> sensitivity of primary production relates to dissimilarities in inorganic carbon acquisition between the major phytoplankton groups. Species-specific differences exist in the predominant carbon source (CO<sub>2</sub> and/or HCO<sub>3</sub><sup>-</sup>) utilized by algal cells, in the affinity for CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> uptake, and in the degree of regulation of the cellular CO<sub>2</sub> concentrating mechanism. Rising CO<sub>2</sub> is therefore expected to increase the competitive advantage of low affinity CO<sub>2</sub>-dependent phytoplankton. As the predominant phytoplankton groups, such as diatoms, coccolithophores and cyanobacteria, appear to differ in CO<sub>2</sub> sensitivity, rising CO<sub>2</sub> may shift the abundance of phytoplankton functional groups and their relative contribution to global ocean productivity.

On the plankton community level, high CO<sub>2</sub> has been found to cause enhanced organic carbon production during the course of phytoplankton blooms. In mesocosm experiments this has generated a steady increase in the organic matter C/N and C/P ratios from glacial, to present, to year 2100 CO<sub>2</sub> levels. This CO<sub>2</sub> fertilization effect has the potential to increase CO<sub>2</sub> sequestration in the ocean, which also would serve as a negative feedback to anthropogenic CO<sub>2</sub> increase.

In a high-CO<sub>2</sub> world these direct CO<sub>2</sub>-related responses will be complicated by effects related to global warming, which causes changes in surface-ocean stratification, insulation, and deep water nutrient supply. In addition, rising sea surface temperatures will directly influence upper ocean metabolic processes, with possible consequences for the balance between auto- and heterotrophy. An integrated assessment of CO<sub>2</sub>- and temperature-related effects on the marine biota is urgently needed in order to achieve a quantitative understanding of the biological responses and related changes in oceanic carbon fluxes under high CO<sub>2</sub> conditions.

### **Impacts on ocean life in a high-CO<sub>2</sub> world**

**Yoshihisa Shirayama**, Haruko Kurihara, Hisayo Thornton, Taiji Yamamoto, Mitsuru Ohta, Kikuo Okita and Shinji Shimode  
Seto Marine Biological Laboratory, Kyoto University  
E-mail: yshira@bigfoot.com

It is necessary to consider two factors when we consider the future high-CO<sub>2</sub> world. One is global warming, that was extensively discussed so far. The other is the direct impact of acidification of seawater on shallow water marine life. Assuming that the future pCO<sub>2</sub> in the atmosphere will reach to 750 ppmv, pH of the seawater is assumed to be about 7.8, which is 0.3 point lower than now. So far, studies regarding the impact of acidification of the seawater on marine organisms focused on the acute lethal impact. In this respect, little impact has been found when pH of the seawater becomes 0.3 point lower. However, to understand the future impact of high PCO<sub>2</sub> on

marine ecosystem, it is necessary to study the chronic and sublethal impact of slight changes of CO<sub>2</sub> on marine ecosystem. Here we report results of a long-term experiment (6 months) under a condition simulating the future high-CO<sub>2</sub> world (550 ppmv) to understand the slight change of chemical condition of seawater on marine life. We used mainly sea urchins in the experiment assuming they are the most sensitive to the acidification of seawater, because they have calcareous skeletons that may dissolve due to acidification of the seawater, there is no barrier between ambient sea water and internal body cavity, and their surface area is extremely large compared to other marine species. As results, we found that after three months, the growth of sea urchins exposed to higher CO<sub>2</sub> was significantly lower than control animals, and after 6 months, the body weight became less than the beginning. We also found that the fertilization rate and growth of embryos of the sea urchin became significantly worse than control animals in high-CO<sub>2</sub> condition, and the impact became stronger with increase of pCO<sub>2</sub>. In the experiments using copepods as a representative of zooplankton, we found that under a condition at which no lethal impact was observed, reproductive activity of animals was completely blocked. All these results strongly suggest that every possible effort should be taken so as to limit increase of atmospheric pCO<sub>2</sub> in the future.

### **Glacial-interglacial transitions as analogs for our high-CO<sub>2</sub> future**

**Robbie Toggweiler**<sup>1</sup> and Joellen Russell<sup>2</sup>

<sup>1</sup>Geophysical Fluid Dynamics Laboratory, P.O. Box 308, Princeton NJ 08542, USA  
E-mail: Robbie.Toggweiler@noaa.gov

<sup>2</sup>Atmospheric and Oceanic Sciences Program, Princeton University, Princeton, NJ  
USA

Climate system models are predicting that the polar oceans will receive more precipitation and run-off in our high- CO<sub>2</sub> future than they do at present. As a result, the polar oceans are supposed to become more stratified and less well-ventilated. The Earth experienced a similar kind of high- CO<sub>2</sub> future as it emerged from the last ice age. The extra CO<sub>2</sub> in this case was vented from the ocean to the atmosphere. Paleo observations suggest that the polar oceans changed in precisely the opposite way. The Southern Ocean, in particular, was more stratified in the cold glacial climate that preceded the glacial-interglacial transition. The fact that the ocean vented CO<sub>2</sub> to the atmosphere during the transition is a direct indication that the Southern Ocean became less stratified as the climate warmed. Why does this paleo analog disagree so sharply with the model predictions?

We would maintain that the transition from glacial to interglacial was brought about through a physical feedback that is missing or is very weak in current climate system models. The feedback links tropospheric temperatures, atmospheric CO<sub>2</sub>, and the mid-latitude westerly winds. Warmer temperatures and higher CO<sub>2</sub> are associated, in particular, with mid-latitude westerlies that are shifted poleward into a tighter annular flow about the poles. Stronger westerlies close to the poles produce ocean currents that carry fresh surface waters away from the poles toward low latitudes. It is this change in wind forcing, we argue, that offsets or overrides the tendency of the polar oceans to become fresher and more stratified in a warmer climate. The westerlies in

the Southern Hemisphere have shifted poleward and strengthened over the last 40 or 50 years in accord with this argument. This means that the polar oceans may well be less stratified, better ventilated, and have a more vigorous circulation in our high- CO<sub>2</sub> future.

### **Ecological effects of deep-ocean CO<sub>2</sub> enrichment: Insights from natural high-CO<sub>2</sub> habitats**

**Eric Vetter**<sup>1</sup> and Craig R. Smith<sup>2</sup>

<sup>1</sup>Marine Science, Hawaii Pacific University, 45-045 Kamehameha Hwy, HI 96744, USA

<sup>2</sup>Department of Oceanography, University of Hawaii at Manoa, 1000 Pope Rd, Honolulu, HI, 96822 USA

E-mail: evetter@hpu.edu

Geological processes may produce sustained natural emissions of CO<sub>2</sub> at the deep-sea floor. For example, hydrothermal vents on Loihi seamount near Hawaii annually emit 5,000-100,000 tons of CO<sub>2</sub> at water depths of 1200 m, yielding CO<sub>2</sub> concentrations as high as 418 mol/m<sup>3</sup>. Because CO<sub>2</sub> is the dominant toxic component of these vent fluids, Loihi provides an extraordinary setting in which to explore the effects of sustained, elevated CO<sub>2</sub> on deep-sea organisms and ecological processes.

Mobile scavengers are important biomass components and organic-matter recyclers in deep-sea ecosystems. We used the PISCES IV submersible to manipulate baited traps and bait parcels in Loihi's CO<sub>2</sub> plume to explore the effects of elevated CO<sub>2</sub> on typical deep-sea scavengers. Lysianassid amphipods and synphobranchid eels were unusually abundant in the vicinity of Loihi's vents, implying that Loihi's rising plume may enhance the flux of carrion to the deep-sea floor.

Baited trap experiments (n = 5) revealed that amphipods exposed to diluted vent waters with a mean pH of 6.3 (background pH of 7.11) and temperature of 5.0°C (background 3.7°C) became intoxicated within 15 minutes and fell to the bottom of the traps. When the experiments were terminated after one hour of exposure, all amphipods revived within 30 minutes and remained active until warmed to 10°C during submersible ascent to the ocean surface.

Open bait parcels placed in similar CO<sub>2</sub> plumes were avoided by amphipods, synphobranchid eels, and hexanchid sharks (i.e., normal deep-sea scavengers). However, baits in plumes did attract vent-specialist bresiliid shrimp, which appeared unaffected by the elevated CO<sub>2</sub>, but consumed parcels at very low rates.

Our combined results suggest that scavenging deep-sea lysianassids and synphobranchids might detect and avoid intoxicating levels of CO<sub>2</sub> resulting from deep-ocean injection of CO<sub>2</sub>, but that specialized components of the deep-sea fauna (e.g., some bresiliid shrimp) may be well adapted to exploit carrion accumulating on the periphery of injection sites. Our experiments also highlight the potential utility of natural CO<sub>2</sub> plumes for exploring the impacts of sustained CO<sub>2</sub> injection on seafloor and water-column ecological processes including recruitment, succession, and material recycling.

## **Overview: CO<sub>2</sub> sequestration by ocean fertilization.**

### **Andrew J. Watson**

School of Environmental Sciences, University of East Anglia,  
Norwich NR4 7TJ, United Kingdom

E-mail: a.j.watson@uea.ac.uk

The idea that fertilization of the ocean by iron addition could be a useful method of removing CO<sub>2</sub> from the atmosphere was first suggested, almost as a joke, by John Gribbin in 1988. Since then, an increasingly large number of observations, experiments and theory have confirmed that iron addition can indeed have a powerful fertilizing effect, especially on the “HNLC” ocean ecosystems (broadly, the equatorial Pacific, northern North Pacific and Southern Oceans). However, fierce debate continues over the wisdom, ethics, efficacy and practicality of fertilization as a method of CO<sub>2</sub> sequestration. A few entrepreneurs have actively promoted it, but most marine scientists remain doubtful for one reason or another, being both sceptical that it will work and concerned about the unintended side effects of its large scale use.

Many facts are not in dispute; addition of iron in the HNLC ecosystems results in stimulation of primary productivity by promoting the growth of diatoms – there is an ecosystem shift towards larger, potentially fast-growing, cells. Associated with this is drawdown of unused nutrients at the surface and CO<sub>2</sub> concentrations. This results in a stronger “biological pump for atmospheric CO<sub>2</sub>, and this is probably important in helping to explain past climate change. However, there is a limitation to how much the ocean uptake of CO<sub>2</sub> can be increased by fertilization. Because there is rapid exchange between the Southern Ocean surface and the deep sea, the Southern Ocean would be the most efficient place to perform such fertilization, but even if the maximum possible programme of fertilization were undertaken there, the increased rate of uptake of CO<sub>2</sub> from the atmosphere would be only a few tenths of a gigaton per year. Compared to the rate at which humans are currently emitting fossil fuel CO<sub>2</sub> (~7 GtC yr<sup>-1</sup>) this is small, so ocean fertilization cannot “solve” the greenhouse problem. It could perhaps be a component of a much larger strategy to tackle the problem however. Compared to tree-planting for instance, a method generally thought to be environmentally acceptable, it looks quite efficient as a sequestration technique.

In my overview I will highlight some of the remaining questions to be answered before it would be sensible to begin a fertilization programme with the purpose of sequestering carbon from the atmosphere. Simply writing these down suggests the kinds of experiments and observations needed to move forward on this issue.

1. Practical; how well does it work? Though it is comparatively easy to fertilize the surface ocean and show an effect on the dissolved CO<sub>2</sub> concentrations, it is much more difficult to document how much (if any) CO<sub>2</sub> is actually taken up from the atmosphere. Practically, to do this would require trials in which a patch of fertilized water was monitored for months or years to determine its fate, by satellite, in-situ instruments measuring the CO<sub>2</sub> and other parameters, and sediment traps documenting the biological export (but note that, contrary to the assumptions in much of the literature, sequestration can occur without any net export).

2. Side effects: these could be both biogeochemical and ecological. For example, there is now some evidence for some water-column production of nitrous oxide during iron fertilization, and this could partially offset any advantage gained by CO<sub>2</sub> sequestration. More difficult to quantify are ecological effects of iron fertilization at higher trophic levels that would be considered undesirable, such as negative impacts on marine mammals. It would be absolutely essential to have knowledge of these potential side effects, which again would require substantial “trial” experiments lasting many years.
3. Ethical: The ethical issues centre on who has the right to use international waters – a global commons – for carbon sequestration by fertilization. Should it, for example, be open to anyone on a first-come-first served basis, based on the profit motive? Unless regulated by international laws and treaties, this is currently the way in which the open ocean is exploited. However, many are of the opinion that the resulting impact (on fisheries for example), has been catastrophic for ocean ecosystems.



# **AN INTRODUCTION TO THE DISCUSSION SESSIONS**

## **Aims of the Discussion Sessions**

The discussion sessions are designed to encourage open discussion on areas of research needed to increase our understanding of the biological and chemical effects in the ocean of increasing atmospheric CO<sub>2</sub> concentrations. Participants will be asked to:

- Identify and prioritise key research questions
- Identify what we need to know to answer those questions and what are the impediments to success (if any)
- Identify promising approaches, including necessary observations, methods, emerging technologies, tools, and regional considerations/scales of study
- Identify the international collaborations and linkages required to answer the key research questions, including linkages to existing international research projects.

The results of the discussions will be summarized in a document to be posted on the Web and distributed to research managers worldwide.

## **Discussion Sessions**

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Monday, 15:00 - 16:00

Identification of Research and Observation Priorities and Approaches - opening discussions.

Wednesday, 9:00 - 12:30

Identification of Research and Observation Priorities and Approaches – continued discussion, conclusions, and drafting

14:00 - 16:00

Report from Discussion Sessions and General Discussions

## POSTER ABSTRACTS

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### TOPIC 1

#### Effects of anthropogenic CO<sub>2</sub> increase on ocean chemistry

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##### The impact of anthropogenic CO<sub>2</sub> on the CaCO<sub>3</sub> System in the oceans

Richard A. Feely<sup>1,\*</sup>, Christopher L. Sabine<sup>1</sup>, Kitack Lee<sup>2</sup>, Will Berelson<sup>3</sup>, Joanie Kleypas<sup>4</sup>, Victoria J. Fabry<sup>5</sup>, and Frank J. Millero<sup>6</sup>

<sup>1</sup>Pacific Marine Environmental Laboratory, NOAA, Seattle, WA 98115-6349, USA

<sup>2</sup>School of Environmental Science and Engineering, Pohang University of Science and Technology, San 31, Nam-gu, Hyoja-dong, Pohang, 790-784, Republic of Korea

<sup>3</sup>Dept. Earth Sciences, University of Southern California, Los Angeles 90089-0740, USA

<sup>4</sup>Environmental and Societal Impacts Group, National Center for Atmospheric Research, Boulder, CO 80307-3000, USA

<sup>5</sup>Dept. of Biological Sciences, California State University San Marcos, San Marcos, CA 92096-0001, USA

<sup>6</sup>University of Miami/Rosenstiel School of Marine and Atmospheric Sciences, Miami, Florida, USA

E-mail: Richard.A.Feely@noaa.gov

Recent evidence suggests a substantial dissolution of calcium carbonate (CaCO<sub>3</sub>) particles in the upper ocean. This shallow-water dissolution of CaCO<sub>3</sub> is in contrast with the paradigm of their conservative nature at shallow water depths. Here, we estimate the in situ CaCO<sub>3</sub> dissolution rates for the global oceans from total alkalinity and chlorofluorocarbon data and also discuss the future impacts of anthropogenic CO<sub>2</sub> on CaCO<sub>3</sub> shell-forming species. Calcium carbonate dissolution rates, ranging from 0.003–1.2 μmol kg<sup>-1</sup> yr<sup>-1</sup>, are observed beginning near the aragonite saturation horizon. The total water-column CaCO<sub>3</sub> dissolution rate for the global oceans is approximately 0.5 ± 0.2 Pg CaCO<sub>3</sub>-C yr<sup>-1</sup>, which is approximately 45–65% of the export production of CaCO<sub>3</sub>.

##### Simulating the CaCO<sub>3</sub> counter pump in the greenhouse

Christoph Heinze

Bjerknes Centre for Climate Research, Geophysical Institute, University of Bergen, Allégaten 70, N-5007 Bergen, Norway

The biogeochemical ocean general circulation model HAMOCC (Maier-Reimer, 1993; Hofmann et al., 2000) is forced with varying external sources for atmospheric CO<sub>2</sub> in order to quantify the respective real world response in biogenic CaCO<sub>3</sub> production using the findings of existing laboratory experiments (e.g., Riebesell et al., 2000). The global model has a resolution of 3.5x3.5 degrees and 22 layers. It simulates the marine nutrient, oxygen and carbon cycles through basic process parameterisations and uses the velocity field of a dynamical general circulation model. Using the standard IPCC CO<sub>2</sub> emission scenario A1B and a levelling off of the emission rates at the value for year 2100, the model predicts a 50% reduction in the global biogenic CaCO<sub>3</sub> export production rate around year 2250. Given that no

interactions with the marine particle flux occur, the respective influence on the CO<sub>2</sub> airborne fraction is small. However, the projected change in biocalcification indicates the potential for a major large-scale perturbation of marine ecosystems.

Next to the reduction in biogenic CaCO<sub>3</sub> production, the model predicts the temporal and spatial pattern of the evolving pH change in response to changes in atmospheric CO<sub>2</sub> concentrations (cf. Caldeira and Wickett, 2003). The projected potential relative changes in pH and CaCO<sub>3</sub> production are largest at high latitudes, suggesting an appropriate monitoring of the biogeochemical marine carbon system specifically for the polar oceans.

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## **A decrease of the CO<sub>2</sub> sink in the North Atlantic**

Nathalie Lefèvre<sup>1</sup>, Andrew J. Watson<sup>1</sup>, Are Olsen<sup>2,3</sup>, Aida F. Ríos<sup>4</sup>, Fiz F. Pérez<sup>4</sup>, Truls Johannessen<sup>2,3</sup>

<sup>1</sup> School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom

<sup>2</sup> Geophysical Institute, University of Bergen, Allégaten 70, 5007 Bergen, Norway

<sup>3</sup> Bjerknes Centre for Climate Research, University of Bergen, Allégaten 55, 5007 Bergen, Norway

<sup>4</sup> Instituto de Investigaciones Mariñas, Consejo Superior de Investigaciones Científicas, Eduardo Cabello 6, 36206 Vigo, Spain

E-mail: n.lefevre@uea.ac.uk

Global ocean carbon models and available syntheses of the oceanic CO<sub>2</sub> flux suggest that the North Atlantic subpolar gyre (50°N-70°N, 80°W-10°W) is a region of increasing uptake of CO<sub>2</sub> from the atmosphere, with the oceanic partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) increasing more slowly than the atmospheric CO<sub>2</sub> over time.

As part of the European project CAVASSOO (Carbon Variability Studies by Ships of Opportunity), available CO<sub>2</sub> data have been gathered in a relational database for the North Atlantic Ocean, which includes over 220 cruises carried out from 1981 to present. We used this database to examine the temporal evolution of seawater pCO<sub>2</sub> in the North Atlantic subpolar gyre (50°N-70°N, 80°W-10°W) where over 100,000 underway seawater pCO<sub>2</sub> measurements have been collected during 1981-1998.

Available CO<sub>2</sub> data are unevenly distributed in both space and time, even for the relatively well-sampled North Atlantic. In order to obtain unbiased estimates, we determined empirical relationships that allow interpolation in time and space. We subdivided the North Atlantic into smaller regions where the seawater pCO<sub>2</sub> could be considered as subject to the same processes and we performed monthly multivariable

linear regressions between pCO<sub>2</sub>, and longitude, latitude, sea surface temperature and year.

Our analysis of available CO<sub>2</sub> data shows that seawater pCO<sub>2</sub> has increased faster than the atmosphere in recent decades, especially in summer, resulting in a decrease in uptake from the atmosphere. A decrease in the biological productivity of the region may be the underlying cause of this trend.

### **Future of CO<sub>2</sub> Uptake in the Bay of Bengal: Potential Impact of the River Interlinking Project of India and the Yarlung-Zangbo Dam of China**

Chandan Mahanta, R. K. Goswami and U. Dutta  
Department of Civil Engineering, Indian Institute of Technology-Guwahati  
Guwahati 781039, INDIA  
mahanta\_iit@yahoo.com

The colossal water ( $1.6 \times 10^{12}$  m<sup>3</sup>/y) and sediment ( $1.4 \times 10^9$  tons, one of the highest in the world) injected from the *Brahmaputra-Ganges* during the southwest monsoon is phenomenon of critical consequence to the air-sea CO<sub>2</sub> flux variability of the BOB. Impact of this episodic pulse of more than 5% of the global dissolved and particulate riverine C load is perhaps the most important of the natural and human induced interactive forcings influencing future capacity of CO<sub>2</sub> assimilation of the Indian Ocean.

Bay of Bengal is one of the high productive areas of the world oceans and very high organic carbon fluxes of more than  $3 \text{ g m}^{-2}\text{y}^{-1}$  have been recorded in sediment trap experiments. On the other hand, based on actual measurements, the final transfer of particulate organic carbon (POC) through the Brahmaputra at the estuary was estimated as  $8 \times 10^6$  tons/year to  $12 \times 10^6$  tons/year.

The northern Indian Ocean as the ultimate sink for exponentially growing CO<sub>2</sub> emission from South Asia and South East Asia is currently under threat of potential reduction in the seasonal sink. The river-linking megaproject of India and the proposed Zangbo-Yarlung dam of China, have enhanced the uncertainty about the future effect of the *Brahmaputra-Ganges* on the processes of the Indian Ocean. If these two biggest projects of human history materialize, Indian Ocean will starve of the current carbon flux with serious impact on the air-sea CO<sub>2</sub> fluxes and anthropogenic CO<sub>2</sub> inventories.

Comparison with the Arabian Sea (where reduction of river discharge over 150 years took place) indicates that such large-scale transition can lower biological carbon uptake by more than 10%. Air-sea CO<sub>2</sub> flux variability impact due to such variations in entrained terrestrial input could be more pronounced than surface temperature or wind speed.

Large uncertainty already exists concerning uptake of carbon by the Indian Ocean due to insufficient knowledge of processes controlling carbonate chemistry. The settling of particulate organic carbon decreases the total C and pCO<sub>2</sub> of the surface layers, whereas the removal of carbonate from surface waters aids in increasing atmospheric

CO<sub>2</sub> by shifting the carbonate equilibria. The differences in the initial production ratio of calcium carbonate to organic carbon can affect significant variations in atmospheric CO<sub>2</sub>.

The profound change to be brought about by this mammoth human impact cutting down the immensity of material transport to the BOB would have critical implications to the capacity of the Indian Ocean, largely mediated by rapidly sinking particles. Changes in the ocean circulation due to reduced stratification would drastically change future anthropogenic CO<sub>2</sub> uptake. While carbon flux between upper and mesopelagic layers would be affected, it would be the reduced net flux of C that will control the ocean-climate interaction. Any abnormal change in the ratio of carbon load into the microbial food chains would lead to destruction of the ecosystem.

### **Inter-comparison of the anthropogenic CO<sub>2</sub> estimates in the northern Indian Ocean**

Chalard Mathieu, Touratier Franck, and Goyet Catherine  
BDSI, Université de Perpignan, 52 avenue Paul Alduy, 66860 Perpignan, France  
E-mail: cgoyet@univ-perp.fr

Using data from the northern Indian Ocean along the WOCE I1 section, Coatanoan et al. (2001) compared the distributions of anthropogenic CO<sub>2</sub> as computed from (1) the  $\Delta C^*$  method (Sabine et al., 1999), and (2) the MIX approach (Goyet et al., 1999). In the present study, the first objective is to compare these previous results with those of a third new independent approach (the TrOCA method; Touratier and Goyet, 2004), using exactly the same dataset. The second objective is to compare the distributions of anthropogenic CO<sub>2</sub> with that of tritium (<sup>3</sup>H; this tracer is used for the first time along section I1).

The results of the TrOCA approach confirm the results of the MIX approach and suggest that the  $\Delta C^*$  approach overestimates the concentration of anthropogenic CO<sub>2</sub> in the layers between 200 and 600 m. This conclusion is further reinforced by the results of the <sup>3</sup>H distribution. In this poster, the results of this inter-comparison exercise are objectively detailed and commented.

## The oceanic sink for anthropogenic CO<sub>2</sub>: Past, present, and future

Christopher L. Sabine<sup>1</sup>, Richard A. Feely<sup>1</sup>, Nicolas Gruber<sup>2</sup>, Robert M. Key<sup>3</sup>, Kitack Lee<sup>4</sup>, John L. Bullister<sup>1</sup>, Rik Wanninkhof<sup>5</sup>, C.S. Wong<sup>6</sup>, Douglas W.R. Wallace<sup>7</sup>, Bronte Tilbrook<sup>8</sup>, Frank J. Millero<sup>9</sup>, Tsung-Hung Peng<sup>5</sup>, Alexander Kozyr<sup>10</sup>, Tsueno Ono<sup>11</sup>, and Aida F. Rios<sup>12</sup>

<sup>1</sup>NOAA Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115, USA.

<sup>2</sup>University of California Los Angeles, IGPP & Department of Atmospheric and Oceanic Sciences, Los Angeles, CA 90095, USA

<sup>3</sup>Princeton University, AOS Program, Forrestal Campus/Sayre Hall, Princeton, NJ 08533, USA

<sup>4</sup>Pohang University of Science and Technology, San 31, Nam-gu, Hyoja-dong, Pohang 790-784, South Korea

<sup>5</sup>NOAA Atlantic Oceanographic and Meteorological Laboratory, 4301 Rickenbacker Cswy., Miami, FL 33149, USA

<sup>6</sup>Institute of Ocean Sciences, Climate Chemistry Laboratory, PO Box 6000, Sidney, B.C. V8L 4B2, Canada

<sup>7</sup>Universität Kiel, Institut fuer Meereskunde, Duesternbrooker Weg 20, D-24105 Kiel, Germany

<sup>8</sup>CSIRO Marine Research and Antarctic Climate and Ecosystem CRC, Hobart 7001, Australia

<sup>9</sup>University of Miami, RSMAS-Div. of Marine and Atm. Sciences, 4600 Rickenbacker Causeway, Miami, FL 33149, USA

<sup>10</sup>CDIAC, Oak Ridge National Laboratory, U.S. Department of Energy, Mail Stop 6335, Oak Ridge, TN 37831-6335, USA

<sup>11</sup>FRSGC/IGCR, Sumitomo Hamamatsu-cho, bldg. 4F, 1-18-16 Hamamatsutyo, Minato-ku, 105-0013, Japan

<sup>12</sup>Instituto de Investigaciones Marinas.CSIC, c/Eduardo Cabello, 6, 36208 Vigo, Spain

E-mail: Chris.sabine@noaa.gov

Using inorganic carbon measurements from an international survey effort in the 1990s consisting of 9618 hydrographic stations collected on 95 cruises and a tracer-based separation technique ( $\Delta C^*$ ), we estimate a global oceanic anthropogenic CO<sub>2</sub> sink for the period from 1800 to 1994 of 118±19 Pg C. Variations in surface concentrations of anthropogenic CO<sub>2</sub> are related to the length of time that the waters have been exposed to the atmosphere and to the buffer capacity, or Revelle Factor, for seawater. Currently, approximately 30% of the anthropogenic CO<sub>2</sub> is found shallower than 200 m and nearly 50% above 400 m depth. The global average depth of the 5 μmol kg<sup>-1</sup> contour is 1000 m. Approximately 60% of the inventory is found in the Southern Hemisphere. The oceanic sink accounts for ~48% of the total fossil fuel and cement manufacturing emissions between 1800 and 1994, implying that the terrestrial biosphere was a net source of CO<sub>2</sub> to the atmosphere of about 39±28 Pg C for the period. By contrast, over the last 20 years the net terrestrial biosphere is thought to be a sink for anthropogenic CO<sub>2</sub> of about 15±9 Pg C. Over the last 20 years, the percentage of anthropogenic emissions taken up by the oceans appears to be smaller than over the last 200 years. Will the future oceans be as efficient at taking up anthropogenic CO<sub>2</sub>? The ocean today only contains about 15% of the anthropogenic CO<sub>2</sub> it could have absorbed if the whole ocean were equilibrated with the current

atmospheric CO<sub>2</sub> perturbation, so there is still a great potential to take up anthropogenic CO<sub>2</sub>. On the other hand, future changes in ocean circulation, chemistry, and biology will have feedbacks on the uptake potential of the ocean.

## TOPIC 2

### Effects of anthropogenic CO<sub>2</sub> increase on ocean biology

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#### Delayed and reduced coccolithophorid calcification under elevated pCO<sub>2</sub>

B. Delille<sup>1</sup>, J. Harlay<sup>2</sup>, I. Zondervan<sup>3</sup>, L. Chou<sup>2</sup>, R. Wollast<sup>2</sup>, A.V. Borges<sup>1</sup>, M. Frankignoulle<sup>1</sup>, U. Riebesell<sup>3</sup>, and J.-P. Gattuso<sup>4</sup>

<sup>1</sup>Unité d'Océanographie Chimique, Université de Liège

<sup>2</sup>Laboratoire d'Océanographie Chimique Géochimie des Eaux, Université Libre de Bruxelles

<sup>3</sup>Leibniz Institut für Meereswissenschaften, Universität Kiel

<sup>4</sup>Laboratoire d'Océanographie de Villefranche

E-mail: Bruno.Delille@ulg.ac.be

Numerous experiments to date have demonstrated that elevated  $PCO_2$  is detrimental to biogenic calcification rates. However, most of these experiments have been realized in batch or continuous cultures and give little information on the dynamics of calcification in natural conditions. The present work describes the development and decay of a nutrient-induced bloom of the coccolithophorid *Emiliana huxleyi* in a mesocosm experiment. Monitoring of Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TAlk) within the seawater enclosures allowed us to describe comprehensively day-to-day dynamics of both calcification and organic carbon production. Three atmospheric  $PCO_2$  conditions (glacial, present and next century) were simulated by bubbling CO<sub>2</sub> mixtures, while total alkalinity was left to evolve from its present value. No conspicuous changes of Net Community Production under elevated  $PCO_2$  were observed, while the production of inorganic carbon appeared to be affected in two ways. Firstly, the production rate of inorganic carbon appeared to be lowered by 40% in the next-century  $PCO_2$  conditions, decreasing concomitantly the calcification-to-photosynthesis ratio from 0.75 (glacial conditions) to 0.45 (next-century conditions). Secondly, the onset of calcification was delayed by 24~48h under elevated  $PCO_2$  conditions reducing the overall length of calcification in the course of the bloom. These two effects would act to reduce the amount of precipitated CaCO<sub>3</sub> by coccolithophorids in a high-CO<sub>2</sub> world.

## **Biogeochemical implications of calcification and secondary production of a population of the brittle star *Acrocnida brachiata* in a temperate coastal ecosystem**

Harlay J.<sup>1</sup>, Gentil F.<sup>2</sup>, and Davoult D.<sup>2</sup>

<sup>1</sup>Océanographie Chimique et Géochimie des Eaux  
Université Libre de Bruxelles, Campus de la Plaine CP 208  
B-1050 (Brussels Belgium)

<sup>2</sup>Station Biologique de Roscoff, UMR 7127 - Equipe Ecologie Benthique  
Université Pierre et Marie Curie (Paris VI), Place Georges Teissier BP 74, F-29682  
Roscoff cedex (France)  
E-mail: jharlay@ulb.ac.be

The production of organic matter and calcium carbonate by a population of the brittle star *Acrocnida brachiata* (Echinodermata) was calculated using demographic structure, population density, and relations between the size and the ash-free dry weight (AFDW) or the calcimass. During a two-year survey in the Bay of Seine (English Channel, France), one of the four major estuaries affecting the biogeochemical cycling of elements in the southern bight of the North Sea, benthic production of this species amounted to 40.3 g.m<sup>-2</sup>.yr<sup>-1</sup> for AFDW and 80.0 g.m<sup>-2</sup>.yr<sup>-1</sup> for CaCO<sub>3</sub>. Respiration, based on secondary production, was estimated to be 736 mmol CO<sub>2</sub>.m<sup>-2</sup>.yr<sup>-1</sup>. Using the molar ratio ( $\psi$ ) of CO<sub>2</sub> released to CaCO<sub>3</sub> precipitated, this biogenic precipitation of calcium carbonate would result in an additional release of 617 mmol CO<sub>2</sub>.m<sup>-2</sup>.yr<sup>-1</sup>. The results of the present study demonstrate that marine calcification should be considered as a significant source of CO<sub>2</sub> to seawater and thus a potential source of CO<sub>2</sub> to the atmosphere, emphasizing the important role of the biomineralization and dissolution in the carbon budget of temperate coastal ecosystems. This additional biogenic source of CO<sub>2</sub> could increase in the future in two ways: firstly, as a positive feedback of  $\psi$  to the rising pCO<sub>2</sub> and, secondly, as a positive response to the availability of nutrients due to eutrophication.

## **Reduction of coral calcification from CO<sub>3</sub><sup>2-</sup> decreases by the mid-21<sup>st</sup> Century**

Chris Langdon and Marlin J. Atkinson

Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964  
Hawaiian Institute of Marine Biology, Kaneohe, HI 96744  
E-mail: langdon@ldeo.columbia.edu

An investigation was conducted to determine how the impact of elevated CO<sub>2</sub> on coral physiology varies over the annual cycle. Experiments were performed in an outdoor, open-top flume located at the Hawaiian Institute of Marine Biology, Kaneohe, HI. Experiments were conducted in January and August so as to obtain data during the annual minima and maxima in water temperature and solar irradiance. Water temperature and PAR irradiance averaged 27.3°C and 37 E m<sup>-2</sup> d<sup>-1</sup> during the August 1999 experiments and 23.4°C and 19 E m<sup>-2</sup> d<sup>-1</sup> during the January 2000 experiments. A mixed assemblage of corals common to Kaneohe Bay were placed in the flume to create a 2.2 m<sup>2</sup> patch of densely packed coral designed to simulate a patch of reef with 100% coral cover. A pump was used to maintain a flow of water of 20 cm s<sup>-1</sup> over the rough-bottom, coral community so as to generate turbulence at the



coral-water interface characteristic of that found on a natural reef. The rate of net photosynthesis under ambient light and seawater chemistry was  $23 \pm 8$  in January and  $45 \pm 3$   $\text{mmol C m}^{-2} \text{ d}^{-1}$  in August. The rate of calcification did not change significantly,  $15.4 \pm 0.8$  vs.  $16 \pm 2$   $\text{mmol CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ , between January and August. In August, the corals were exposed to seawater with a  $\text{pCO}_2$  of 460  $\mu\text{atm}$  in the ambient experiments and 789  $\mu\text{atm}$  in the acid-treated experiments. The corresponding concentrations of  $\text{CO}_3^{2-}$  were 185 and 113  $\mu\text{mol kg}^{-1}$ . In January, there were two levels of  $\text{CO}_2$  treatment. The  $\text{pCO}_2$  levels were 391, 526 and 781  $\mu\text{atm}$  and the corresponding  $\text{CO}_3^{2-}$  concentrations were 191, 144 and 104  $\mu\text{mol kg}^{-1}$ . The treatments simulate the changes in  $\text{pCO}_2$  and  $[\text{CO}_3^{2-}]$  that could be encountered in the mid-to-late 21<sup>st</sup> Century if  $\text{CO}_2$  emissions continue at the present pace. We found that elevated  $\text{CO}_2$  treatment caused no significant change in net oxygen-based photosynthesis, however, net carbon-based photosynthesis increased by 22% in August and by 39% and 52% in January. Calcification rate decreased by 46% in August and by 24% and 81% in January. The results show that a large decrease in coral calcification in response to elevated  $\text{pCO}_2$  is observed throughout the annual cycle in water temperature and solar irradiance. The hypothesis that an increase in photosynthesis due to an increase in temperature or  $\text{pCO}_2$  would prevent a large drop in coral calcification is not supported by this data set.

### **Elevated carbon dioxide increases carbon fixation by *Emiliana huxleyi***

Nikos Leonardos and Richard J. Geider

Department of Biological Sciences, University of Essex, Colchester CO4 3SQ, Essex, U.K.

E-mail: hernes@essex.ac.uk

The oceans are a significant sink for anthropogenic carbon dioxide. Phytoplankton is important in regulating ocean-atmosphere  $\text{CO}_2$  exchange and the marine carbon cycle on interannual to millennial time scales. Phytoplankton provide a link between the C, N and P cycles in the sea. Following the Intergovernmental Panel on Climate Change IS92a scenario, simulated atmospheric  $\text{CO}_2$  exceeds 1,900 parts per million (p.p.m.) at around the year 2300, about a five-fold increase from present values, with a consequent drop in ocean pH of about 0.77 units. The variability of the strength of the oceanic biological  $\text{CO}_2$  sink is not well understood. Here we show elevated carbon dioxide fixation into organic matter for a non-calcifying strain of the coccolithophore *Emiliana huxleyi*, under elevated atmospheric  $\text{CO}_2$  conditions that are accompanied by elevated C:N and C:P ratios. The degree of elevation of the cellular carbon quota depended on light and type of nutrient limitation. The interaction of these factors on the cellular C, N and P quotas and stoichiometry was investigated. Our data are consistent with the hypothesis that elevated carbon dioxide uptake by phytoplankton such as *E. huxleyi*, following increases in atmospheric  $\text{CO}_2$ , could increase carbon storage in the ocean and act as a negative feedback on atmospheric  $\text{CO}_2$ .

## **Bio-optical impact of phytoplankton on ocean physics and carbon cycle**

Manfredi Manizza<sup>1,2</sup>, Corinne Le Quéré<sup>1</sup>, Andrew J. Watson<sup>2</sup>, and Erik T. Buitenhuis<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Biogeochemie, Postfach D007745, Jena, Germany

<sup>2</sup>University of East Anglia, NR4 7TJ, Norwich, UK

E-mail: mmanizza@bgc-jena.mpg.de

Phytoplankton modify the surface penetration of light and heat, altering upper ocean temperature and stratification. We study this feedback between physical and biological processes and the impact on the ocean carbon cycle. We use OPA, a global Ocean General Circulation Model coupled to a Sea-Ice model (LIM) and to an ocean biogeochemistry model, the Dynamic Green Ocean Model (DGOM).

The DGOM has five Plankton Functional Types, three phytoplankton (nanophytoplankton, coccolithophores and diatoms) and two zooplankton (micro and meso), and co-limitation by phosphate, silicate, iron and light. The DGOM also has a full ocean carbon cycle model.

Globally, the presence of phytoplankton warms the Sea Surface Temperature (SST) by 0.05 °C, increases stratification by 5 m, and reduces the sea ice cover by ca 3%. Regionally, the impact of phytoplankton is much larger. SSTs warm by up to 1.5 °C in spring at high latitudes and ocean surface stratifies up to 30 m. The change of the thermal structure at boundaries of the equatorial Pacific Ocean also modifies the circulation, enhancing the divergence and the upwelling.

The increase in stratification produces an increase in diatoms in the Southern Ocean and in coccolithophores at high latitudes because of the reduction of light limitation. The combined effects of ocean surface warming, enhanced stratification, enhanced upwelling and reduced sea ice cover produce a net CO<sub>2</sub> outgassing equivalent of 0.1 PgC yr<sup>-1</sup>. The increase in stratification causes a decrease in export production by 0.3 PgC yr<sup>-1</sup>.

Future scenarios of high atmospheric CO<sub>2</sub> suggest a general warming of the world ocean which drives significant changes in the pelagic ecosystem. Considering the results obtained here, we argue that full ecosystem-physics feedbacks are required to assess climate impact on ocean carbon cycle.

## **Climate change recovery of coral reef calcification associated with ocean warming**

Ben McNeil and Richard Matear

Centre for Environmental Modeling and Prediction, School of Mathematics,

University of New South Wales, Sydney, NSW, Australia

E-mail: b.mcneil@unsw.edu.au

Coral reef communities require sufficient enough levels of seawater carbonate ion (CO<sub>3</sub><sup>2-</sup>) in order for calcifying organisms to produce its mineral calcium carbonate (CaCO<sub>3</sub>) structure. The aragonite saturation state ( $\Omega_{\text{arag}}$ ) of the ocean is a measure of the ocean's ability to promote calcification and strong evidence has been shown via

laboratory experiments that calcification rates of certain coral species decrease in conjunction with  $\Omega_{\text{arag}}$  (Langdon et al, 2000). However, just as the global coral reef distribution is controlled by temperature, the rate of calcification within numerous coral colonies has also been shown to increase in association with warmer temperatures (Lough and Barnes, 2000). The effects of these two environmental conditions on coral reef calcification counteract each other in association with climate change and up until now, future projections have neglected ocean warming and any potential climate change feedback on  $\Omega_{\text{arag}}$  (Kleypas et al, 2000). Here, we incorporate observed empirical evidence within a coupled atmosphere-ocean carbon cycle model in order to predict future changes in  $\Omega_{\text{arag}}$  and coral reef calcification under climate change. Although  $\Omega_{\text{arag}}$  was found to decrease throughout the 21<sup>st</sup> Century, climate change slows this decrease by ~16% due to a weaker oceanic CO<sub>2</sub> solubility pump. Coral reef calcification decreased by ~9% between 1880 and the mid-1960s, while our predictions suggest corals slowly recover to levels exceeding those of the pre-industrial era (~20%) by the year 2100 due to the effects of an ocean that is on average 2.7°C warmer than during pre-industrial times. Our simulations suggest that coral reef calcification today is equivalent to those levels found in the late 19<sup>th</sup> Century and is in conflict with previous projections suggesting a considerable decrease.

### **Response of the coccolithophorid *Emiliana huxleyi* to elevated pCO<sub>2</sub> under nitrate limitation**

Sciandra, A.,<sup>1</sup> Harlay, J.,<sup>2</sup> Lefèvre, D.,<sup>3</sup> Lemée, R.,<sup>1</sup> Rimmelin, P.,<sup>3</sup> Denis, M.,<sup>3</sup> and Gattuso J.-P.<sup>1</sup>

<sup>1</sup>Laboratoire d'Océanographie, BP 28, 06234 Villefranche-sur-mer Cedex. France

<sup>2</sup>Université Libre de Bruxelles, Belgium

<sup>3</sup>Centre d'Océanologie de Marseille, France

E-mail: gattuso@obs-vlfr.fr

Precipitation of calcium carbonate by phytoplankton in the photic oceanic layer is an important process regulating the carbon cycling and the exchange of CO<sub>2</sub> at the ocean-atmosphere interface. Previous experiments have demonstrated that, under nutrient-sufficient conditions, doubling the partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) in seawater—a likely scenario for the end of the century—can significantly decrease both the rate of calcification by coccolithophorids and the ratio of inorganic to organic carbon production. The present work investigates the effects of high  $p\text{CO}_2$  on calcification by the coccolithophore *Emiliana huxleyi* grown under nitrogen-limiting conditions, a situation that can also prevail at sea. Nitrogen limitation was obtained within NO<sub>3</sub>-limited continuous cultures renewed at the rate of 0.5 d<sup>-1</sup> and exposed to a saturating light level.  $p\text{CO}_2$  was increased from 400 to 700 ppm and controlled by bubbling CO<sub>2</sub>-rich or CO<sub>2</sub>-free air in the cultures. The  $p\text{CO}_2$  shift had a rapid effect on cell physiology that occurs within 2 cell divisions subsequent to the perturbation. Net calcification rate ( $C$ ) decreased by 25%, and, in contrast to previous studies with N-replete cultures, gross community production (GCP) and dark community respiration (DCR) also decreased. These results suggest that the increasing  $p\text{CO}_2$  has no noticeable effect on the calcification/photosynthesis ratio ( $C/P$ ) when cells of *E. huxleyi* are NO<sub>3</sub>-limited.

## Spread of coccolithophores into Arctic Waters? Results from twenty years of satellite observations

Toby Tyrrell<sup>1</sup>, Agostino Merico<sup>1</sup>, Tim Smyth<sup>2</sup>, Peter Miller<sup>2</sup>, Ben Tarrant<sup>3</sup> and Chris Brown<sup>4</sup>

<sup>1</sup>School of Ocean and Earth Science, Southampton Oceanography Centre  
Southampton University, European Way, Southampton SO14 3ZH

<sup>2</sup>Plymouth Marine Laboratory, Prospect Place, West Hoe, Plymouth, PL1 3DH, UK

<sup>3</sup>Department of Geography, University College London, UK

<sup>4</sup>National Environmental Satellite Data and Information Service, NOAA, Camp Springs, Maryland, USA

E-mail: T.Tyrrell@soc.soton.ac.uk

A probable consequence of global warming due to high CO<sub>2</sub> is increasing stratification of high-latitude oceans and consequent changes to phytoplankton assemblages there. The difficulties of sampling a wide ocean with only a few ships mean that such changes may already be occurring but are not being detected. We take advantage of the fact that only one phytoplankton species, the coccolithophore *Emiliana huxleyi*, is distinguishable from space. Because of its unique overproduction of light-scattering coccoliths, blooms of *Emiliana huxleyi* are optically distinct from those of other phytoplankton species. Satellites can detect the high chlorophyll concentrations of other blooms, but cannot determine which species is responsible. We have examined more than twenty years of archived satellite images from (1) the eastern Bering Sea and (2) the Barents Sea. We looked to see if the frequency of blooms of the species *Emiliana huxleyi* is changing in these areas. In both locations SeaWiFS (1997-present) has detected blooms in recent years but CZCS (1978-1986) did not. We carried out a new analysis of black-and-white AVHRR images (in which these blooms can also be seen) from the early 1980s to the present day. We found no evidence of *Emiliana huxleyi* blooms in the eastern Bering Sea before 1996 and therefore the blooms in 1996-2000 appear to have been a new phenomenon in the area. In contrast, for the Barents Sea we found evidence of some earlier blooms in the years 1989-1992, although the continuous appearance of blooms through all of the last six years (1998-2003) was not matched earlier in the record. We compare the bloom records to climatic and stratification indices. If Arctic warming trends continue, coccolithophore blooms may become increasingly frequent in and around the Arctic. This trend could combine with effects of increasing acidification to alter the geographical distribution of coccolithophores in the future.

### TOPIC 3

## Effects of purposeful CO<sub>2</sub> enrichment on ocean chemistry

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### The counter-regulation produced by the Oxygen Minimum Zones (OMZ) formation on CO<sub>2</sub> oceanic sequestration

A. Paulmier<sup>1</sup>, D. Ruiz-Pino<sup>1</sup>, O. Ulloa<sup>2</sup>, L. Farias<sup>2</sup> and A. Poisson<sup>1</sup>

<sup>1</sup>Laboratoire de Biogéochimie et Chimie Marines (LBCM-IPSL), Université Pierre et Marie Curie, Paris, France

<sup>2</sup>Programa Regional de Oceanografía Física y Clima (PROFC-COPAS), Universidad de Concepción, Concepción, Chile

E-mail: paulmier@ccr.jussieu.fr

The OMZ, a potential primitive anoxic ocean persistence, is expanding since the beginning of the 20<sup>th</sup> Century, probably due to both circulation and Primary Production (PP) changes predicted as a global warming effect. A global PP increase through fertilization (Fe) would lead to an OMZ formation by O<sub>2</sub> intense consumption during the remineralization. The OMZ formation could reduce the oceanic capability of CO<sub>2</sub> sequestration, an opposite effect of the artificial fertilization expectations. This study documents the more extended and intense open OMZ, in the Eastern South Pacific, during 4 cruises (2000-2002) and a monthly monitoring (2000-2001).

The OMZ formation corresponds to the “active” phase, associated with strongest O<sub>2</sub> consumption due to an intense remineralization at the shallow oxycline. This OMZ remineralization produces the highest subsurface DIC of the global ocean (2527-2280 μmol/kg) called “New DIC”, acting as a barrier for CO<sub>2</sub> sequestration. This New DIC constitutes a CMZ (Carbon Maximum Zone) which could make the global OMZs represent more than 40% of the atmospheric CO<sub>2</sub> stock. Located near the sea surface, the CMZ could be easily pushed up by an usual OMZ upwelling. So the OMZs through the CMZs should be investigated, because they could contribute to an atmospheric CO<sub>2</sub> increase of: +9±5 ppmv in the modern ocean (similar to the effect produced by burning fuels fossils during 10 years), and +26±23 ppmv from the last Glacial (G) to InterGlacial (IG) transition (25% of the total G-IG increase). The CMZs as an oceanic CO<sub>2</sub> reserve, would have a similar behaviour, but acting in shorter time scales, than fuel fossils stored as petrol.

An additional effect on the radiative GreenHouse Gases (GHG) produced by the fertilized OMZ is due to the well-known intense N<sub>2</sub>O production. Thus the strong production of both GHG (CO<sub>2</sub>, N<sub>2</sub>O) during the modern OMZ formation, contributes to a carbon oceanic source (+10 GtCeq/yr) 5 times higher than the ocean sink, and could help to understand the simultaneous increase of CO<sub>2</sub> and N<sub>2</sub>O observed during the last G-IG transition.

However, to evaluate the total feedback on ocean CO<sub>2</sub> sequestration, the effect of OMZ formation on carbonate system and carbon biological pump through a potential shift in planktonic community (strong -C/O (1.14±0.3) and C/N (14±2.6), decrease of alkalinity and pH) should be carefully overseen. Actually these perturbations, the direct GHG release and a possible metal trap role (producing an auto-fertilization), could deeply mitigate any fertilization strategy.

## Towards the investigation of CO<sub>2</sub> phase transition processes using advanced pressure lab technology

Gregor Rehder<sup>1</sup>, Holger Steffen<sup>2</sup>, and Giselher Gust<sup>2</sup>

<sup>1</sup>IFM-GEOMAR, Leibniz-Institut für Meereswissenschaften, Marine Biogeochemie Dienstgebäude Ostufer, Wischhofstr 1-3, D- 24148 Kiel, Germany

<sup>2</sup>Technische Universität Hamburg-Harburg, Meerestechnik I, Laemmersieth 72, D-22305 Hamburg, Germany

E-mail: grehder@ifm-geomar.de

The purposeful injection and storage of CO<sub>2</sub> is considered as an option to mitigate future increase of the atmospheric CO<sub>2</sub> content. The assessment of the propagation and dissolution behavior of CO<sub>2</sub> is complicated by the potential to form hydrates with water in the depth range suggested for release. Formation of hydrates at the water/CO<sub>2</sub> interface can control the dissolution of droplets and thus affect the depth of CO<sub>2</sub> uptake. Formation of hydrates from CO<sub>2</sub> disposed at the seafloor will affect the longevity of a condensed CO<sub>2</sub> phase as well as its mechanical properties, and will control interaction with the sediments. Though some *in situ* experiments provided first insight in the behavior of liquid CO<sub>2</sub> exposed to oceanic conditions (Brewer et al., 1999 & 2002; Rehder et al., 2004), the understanding of the effects of oceanic conditions and chemical impurities require well-parameterized series of laboratory experiments.

We plan to investigate the near-field behavior of CO<sub>2</sub> injection sites using a pressure lab developed at the TUHH within the last three years. The lab consists of a main cylindrical pressure vessel with an internal volume of 99 L, a diameter of 30 cm and a height of 140 cm, which is rated to 55 MPa. Two optical windows provide visual inspection from outside, and a variety of electrical ports both at the top and the bottom of the vessel allow almost unlimited internal instrumentation (sensors, pumps, motors, cameras, etc.). For the investigation of the behavior of CO<sub>2</sub> in seawater, two different internal set-ups will be used to simulate the hydrodynamic conditions. Phase transitions at the seafloor ( $P > 28\text{MPa}$ ) will be performed using a readily designed and patented microcosm flume (Thomsen and Gust, 2000; Tengberg et al., 2004), which will allow the investigation of CO<sub>2</sub>-dissolution, hydrate formation, and gravitational instability at the liquid CO<sub>2</sub>-hydrate interface under controlled parameterization of T, P, shear stress (i.e. current velocity), and chemical composition. Behavior of rising (or sinking) CO<sub>2</sub> droplets will be performed using a droplet-focusing vertical flow chamber.

This experimental work is planned and embedded in the CARBO-OCEAN integrated project proposed within the EU 6<sup>th</sup> Framework. The small-scale parameters will help to parameterize appropriate meso-scale models (UIB, Norway), which in turn will help to constrain global scale model approaches (LSCE, France).

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### **High CO<sub>2</sub> at the deep-sea hydrothermal systems**

Kiminori Shitashima

Central Research Institute of Electric Power Industry (CRIEPI)

1646 Abiko, Abiko-City, Chiba, 270-1194, JAPAN

E-mail: shita@criepi.denken.or.jp

The ocean sequestration of CO<sub>2</sub> recovered from fossil fuel usage has been studied as one of possible options to mitigate global warming. For considering the possibility of the CO<sub>2</sub> ocean sequestration, it is necessary to examine the environmental impacts of the sequestered CO<sub>2</sub> to the ocean.

Through deep-sea hydrothermal activities, a large amount of elements, including carbon as a form of CO<sub>2</sub>, are discharged to deep ocean. Deep-sea hydrothermal activities occur at the active lithosphere area, such as spreading ridges, back-arc basins and under-sea volcanos. Seawater penetrates downward toward the magma chamber from cracks in oceanic crust, then rapid heating forces the buoyant hot water, hydrothermal fluid, to the surface of seafloor as a hydrothermal vent. The vents of the natural CO<sub>2</sub>-rich fluid and hydrate formation were found in 1989 at the hydrothermal active area in the mid-Okinawa Trough, back-arc basin (Sakai et al. 1990). This fact suggests that CO<sub>2</sub> is discharged to the deep ocean by hydrothermal activities at the seafloor where hydrothermal vents exist. Hydrothermal fluids are highly enriched in CO<sub>2</sub> and show low pH (about pH2-3) relative to seawater. The CO<sub>2</sub> in deep-sea hydrothermal vent fluids is mainly of magmatic origin. This CO<sub>2</sub> is taken up from the basalt by the fluid during high temperature seawater-magma interaction. Furthermore, at the back-arc basins, CO<sub>2</sub> is extracted from organic matter and calcium carbonate in the sediment over the subduction zone is added to the fluids.

Deep-sea hydrothermal systems are optimum as an on-site field analysis for a high CO<sub>2</sub> environment in the deep ocean. In the observation of the hydrothermal CO<sub>2</sub>, it is possible to know the physicochemical behavior and diffusion process of CO<sub>2</sub> in the deep ocean. Furthermore, information on the hydrothermal ecosystem in the high CO<sub>2</sub> environment is important for an environmental impact assessment of the CO<sub>2</sub> ocean sequestration. In my poster presentation, I will report the field observation results of hydrothermal CO<sub>2</sub> at the several deep-sea hydrothermal systems, and the behavior and diffusion of hydrothermal CO<sub>2</sub> in the deep ocean. For example, total CO<sub>2</sub> concentration and pH in the hydrothermal fluid samples of the S-EPR ranged from 16 to 5 mM and from 3.1 to 7.6, respectively. The hydrothermal fluids discharged from the vents were rapidly diluted with ambient seawater; therefore, total CO<sub>2</sub> concentration and pH value in the plume waters become close to that of ambient seawater near the vents.

## TOPIC 4

### Effects of purposeful CO<sub>2</sub> enrichment on ocean biology

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#### **Ocean storage of CO<sub>2</sub>: Monitoring leaks and assessing impacts**

L.G. Golmen<sup>1</sup>, Guttorm Alendal<sup>2</sup>, Reidun Gangstø<sup>2</sup>, and J.A. Berge<sup>1</sup>

<sup>1</sup>Norwegian Institute for Water Research (NIVA), Nordnesboder # 5, 5005 BERGEN, Norway

<sup>2</sup>Bergen Center for Computational Science. University of Bergen, Thormøhlensgt. 55, N-5020 Bergen, Norway

E-mail: lars.golmen@niva.no

Large amounts of CO<sub>2</sub> may be stored either in the deep ocean or in the geological substrata below. The geological storage is assumed to have the longest residence time, but still some CO<sub>2</sub> will eventually escape to the sea above and subsequently either leak to the atmosphere or deposit as carbonates in the sediments. This makes the two reservoir methods similar with respect to the possible impacts on bottom fauna and deep sea dwellers, and in terms of requirements for monitoring the (escaped) CO<sub>2</sub>. The poster describes the fauna communities found in a subset of locations in the NE Atlantic along a depth/species gradient, and various scenarios of CO<sub>2</sub> exposure and impacts. The scenarios are based on numerical model results from A: A submerged direct discharge of CO<sub>2</sub> into the ocean, and B: Diffusive leaks from sub-bottom storage. Based on the results/scenarios, monitoring requirements in terms of sensor capabilities, distribution of sensors in network and communication to shore is described. Suggestions are made for future inclusion of CO<sub>2</sub> monitoring in regional oceanographic networks such as ESONET, and finally the strategy to develop a CO<sub>2</sub> monitoring system through the EU-FP6 NoE 'CO<sub>2</sub>GEONET' is presented.

#### **Influence of hypercapnia on the physiology of the Antarctic eelpout *Pachycara brachycephalum*: A model organism for deep-sea fish**

M. Langenbuch, C. Burgard, C. Bock, H.-O. Pörtner

Alfred Wegener Institute for Polar and Marine Research, Ecophysiology,

Columbusstr., 27568 Bremerhaven, Germany

E-mail: mlangenbuch@awi-bremerhaven.de

Scenarios of rising CO<sub>2</sub> concentrations in surface waters due to atmospheric accumulation of anthropogenic CO<sub>2</sub>, or in the deep sea due to anticipated industrial dumping of CO<sub>2</sub>, suggest that hypercapnia (elevated CO<sub>2</sub> partial pressure, PCO<sub>2</sub>) will become a general stress factor in aquatic environments with largely unknown effects on species survival, especially in cold and deep water.

The aim of the present study was to identify the mechanisms by which increased CO<sub>2</sub> concentration affect the mode of metabolism at different organisational levels of the Antarctic eelpout *P. brachycephalum*. On the one hand, we monitored energy metabolism and circulatory performance of the whole animal by means of oxygen consumption measurements as well as *in vivo* <sup>31</sup>P-NMR-spectroscopy (intracellular pH and adenylate metabolism) and MR imaging of arterial and venous blood flow and



tissue oxygenation in white muscle. On the other hand, we analysed changes in energy and protein metabolism of isolated fish hepatocytes by determining the rates of oxygen consumption at various levels of PCO<sub>2</sub>, of intra- and extracellular pH, and after inhibition of protein synthesis by cycloheximide. While a severe hypercapnia-induced acidosis caused a reduction in aerobic metabolic rate by 34-37% in isolated hepatocytes concomitant to a 80% inhibition of cellular protein synthesis, no such energy-saving strategy could be observed at the whole animal level. In contrast, animals incubated at 1.01 kPa PCO<sub>2</sub> showed a significant increase of oxygen consumption rates 15 hours after the onset of hypercapnia. Intracellular pH decreased at the beginning of the CO<sub>2</sub> exposure but was completely restored within 20 hours. Despite the increased aerobic energy turnover, no hypercapnic effects could be detected on energy status and oxygenation of white muscle or on arterial and venous blood flow.

From the *in vivo* data we conclude that animals do not suffer from acute CO<sub>2</sub> toxicity at 1.01 kPa. However, it needs to be investigated whether long-term tolerance to hypercapnia becomes limiting due to elevated metabolic costs. Besides, elevated PCO<sub>2</sub> may limit the functional integrity of the liver due to a pronounced depression in protein anabolism as seen in isolated hepatocytes *in vitro*.

### **Possible use of stable isotopes for determining alteration of deep-sea ecosystem induced by a high-CO<sub>2</sub> world**

Saeko Mito and Jun Kita

Research Institute of Innovative Technology for the Earth (RITE)

9-2 Kizugawadai, Kizu-cho, Kyoto 619-0292, Japan

E-mail: [kita@rite.or.jp](mailto:kita@rite.or.jp)

Increase of anthropogenic CO<sub>2</sub> in the atmosphere will cause alteration of marine ecosystems through not only global warming but also oceanic CO<sub>2</sub> concentration. On the other hand, implementation of CO<sub>2</sub> ocean sequestration, intended injection of anthropogenic CO<sub>2</sub> into the deep ocean to prevent global warming, could have a significant impact on deep-sea ecosystems. This preliminary study aims at determining the food web structure of deep sea by means of stable isotope ratios ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) of organisms to provide base information necessary for detecting such alterations of the ecosystem.

Zooplankton and micronekton were collected by ORI net at the sub-arctic area (36.41°N; 141.90°E, vertical tow from 1500m to 500m depth) and at the sub-tropic area (22.50°N; 131.91°E, horizontal tow at 500m and 1000m depths) of the western North Pacific in December 2003. Particulate organic matter (POM) was also collected from the depth of 500m and 1000m at sub-tropic area in July 2004. Stable isotope ratios of the samples were analyzed by an EA-IRMS. To avoid variance in  $\delta^{13}\text{C}$  due to lipid content levels of the organisms, the solvent-extractable lipid fractions were removed from samples for  $\delta^{13}\text{C}$  analysis.

The relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of copepods, salps, shrimps and fish at the sub-arctic area was expressed as  $\delta^{15}\text{N} = 2.6\delta^{13}\text{C} + 55.2$ . At the depth of 500m of sub-tropic area, there was no significant relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of

copepods, amphipods, krill, shrimps, arrow worms and fish. On the other hand, at the depth of 1000m of sub-tropic area, the relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of copepods was expressed as  $\delta^{15}\text{N} = 2.7\delta^{13}\text{C} + 58.3$ . We found that  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of POM from both depths did not fit the linear relationship described above. Values of  $\delta^{13}\text{C}$  for POM were significantly lower than that of deep-sea organisms. Therefore, POM as a whole could not be assumed as a primary food for deep-sea zooplankton.

Although further analysis, such as material transport from surface to the deep sea, is needed, the food web structure of mesopelagic zone might be simple because of the limited food source. Analysis of food web structure would be useful for developing a deep-sea ecosystem model. A high- $\text{CO}_2$  world will result in alteration of the trophic position of each organism in the deep sea. It was expected that such an ecosystem alteration could be determined by means of stable isotope ratios of the organism.

## TOPIC 5

### Mitigation Techniques: Methods, Efficiencies, Unknowns

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#### What can we learn from natural iron fertilization of the ocean?

Blain, S.,<sup>1</sup> Quéguiner B.,<sup>1</sup> Jeandel C.,<sup>2</sup> and Park, Y.<sup>3</sup>

<sup>1</sup>LOB, Centre d'Océanologie de Marseille, Campus de Luminy, case 901, F-13288 Marseille cedex 09

<sup>2</sup>LEGOS, Observatoire Midi-Pyrénées, 14, Ave E. Belin, 31400 Toulouse, France

<sup>3</sup>Museum National d'Histoire Naturelle, 43 rue Cuvier, F-75231 Paris, France

E-mail: [stephane.blain@com.univ-mrs.fr](mailto:stephane.blain@com.univ-mrs.fr)

During the last fifty years, more and more evidence has been gathered assessing the major role of iron in the control of the biological pump of  $\text{CO}_2$  in the ocean. Deliberate small-scale iron fertilization experiments in different oceanic regions have unequivocally demonstrated that iron additions enhance primary production and modify the phytoplankton community structure. Despite efforts to increase the duration of these experiments, the impact of iron addition on the export of carbon in deep water is not yet clearly established. Iron fertilizations may also be prone to artifacts due to the limited size of the patch. Simultaneously to these scientific experiments, more worrying large-scale fertilizations planned by private companies are presented like a cheap and easy solution to greenhouse gas control. However, the efficiency and the possible negative effects of such geoengineering solutions are still largely unknown.

Natural iron fertilization occurs in the ocean and is an interesting alternative approach to study the role of iron and its complex interplay with other forcing parameters (light, vertical mixing, and macronutrients). Atmospheric dust deposition is a well-known process of iron enrichment of surface waters but it occurs only occasionally. By contrast, natural iron enrichment of deep water by contact with continental margin followed by upward vertical transport can be considered as a permanent iron source to the surface layer. If such a process occurs in an iron-limited region; a massive bloom

can be generated as long as macronutrients remain available. This would typically be expected in an HNLC environment. Attention has been given to Southern Ocean islands where satellite images have shown a yearly recurrent bloom extending over and eastward of the Kerguelen Plateau. Previous data gathered in this area are consistent with the hypothesis of a bloom induced by iron fertilization. A large pCO<sub>2</sub> decrease (~60 µatm) associated with the bloom was also measured in this area.

Detailed investigations will be carried out in this area during January-February 2005 (KEOPS PROOF/INSU project) onboard N.O. Marion Dufresne (IPEV). This project, associating foreign colleagues (Australia, Belgium, Netherland, New Zealand, U.S.A.), aims at investigating the mechanisms of iron fertilization, quantifying the annual carbon export in a naturally iron fertilized vs. a non-fertilized adjacent area, and identifying possible side effects of Fe fertilization: release of biogenic gases (DMS, N<sub>2</sub>O, CH<sub>4</sub>...), shifts in the community structure of primary producers and related changes in organic matter channeling through the pelagic foodweb.

## TOPIC 6

### Observational Field Programs

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#### **Air-sea CO<sub>2</sub> exchange in the east Indian sector of the Southern Ocean: Preliminary results of the MINERVE program**

E. Brévière<sup>1</sup>, C. Brunet<sup>1</sup>, N. Metzl<sup>1</sup>, A. Poisson<sup>1</sup>, B. Schauer<sup>1</sup>, B. Tilbrook<sup>2</sup>

<sup>1</sup>LBCM/IPSL, Université Pierre et Marie Curie, case 134, 4 place Jussieu, 75252 Paris cedex 05

<sup>2</sup>CSIRO, Div. Oceanography, Marine Lab., GPO Box 1538, Hobart, Tasmania, 7001 Australia

E-mail: breviere@ccr.jussieu.fr

After 5 years of interruption (1997-2002) the MINERVE program is renewed for almost 10 years. In this program, the distribution of carbon dioxide partial pressure (pCO<sub>2</sub>) in surface seawaters of the Southern Ocean is investigated on a repeated section south of Tasmania, Australia (from 43°S to 67°S). Complementary hydrological and biogeochemical parameters such as chlorophyll-*a*, temperature, salinity, dissolved inorganic carbon (DIC), total alkalinity (TA) and nutrients are collected and analyzed on board the *RSV Astrolabe* (IPEV) during repeated cruises of resupplying from Hobart (Tasmania) to Dumont D'Urville (Adelie Land, Antarctica). The measurements are carried out during 3 cruises happening between October and March each year. Five very different provinces are crossed north to south every transect. Consequently, this program allowed observation and parameterization of variations in space and time of pCO<sub>2</sub> in surface seawaters. The MINERVE program follows the earlier work conducted by scientists from Australia, France, Japan and USA in the same area. Since 2003, MINERVE takes part in the ORE/CARAUS program (INSU/IPSL), a long-term observational project, in coordination with SO/OISO program evolving in the western-south Indian Ocean.

We will present preliminary results of the first cruises conducted from October 2002 to March 2003 and discuss the spatio-temporal variability of the CO<sub>2</sub> sources and sinks in relation to large-scale temperature and ocean color anomalies.

### **Seasonal variability of $f\text{CO}_2$ in seawater from the southwest subtropical Atlantic and adjacent continental shelf**

Rosane Gonçalves Ito,<sup>1</sup> Bernd Schneider,<sup>2</sup> and Helmuth Thomas<sup>2</sup>

<sup>1</sup>Instituto Oceanográfico, University of São Paulo, São Paulo-SP, Brazil.

<sup>2</sup>Institut für Ostseeforschung Warnemünde, University of Rostock, Warnemünde-Rostock, Germany.

E-mail: rgito@io.usp.br

Measurements of sea surface  $f\text{CO}_2$ , salinity, *in situ* temperature, nutrients and chlorophyll-a were made aboard the R.V. “Prof. W. Besnard”, in October/November 1997, January/February, and June 1998, during the “Ocean Circulation in the Southwest Atlantic Region” program (COROAS). The T-S distribution in each sampling season showed that the surface water mass was the Tropical Water (TW), and Coastal Water (CW) with strong influence of the TW on the continental shelf in the summer and winter cruises. The open ocean presents  $f\text{CO}_2(\text{sw})$  values of 362.8  $\mu\text{atm}$  ( $\Delta f\text{CO}_2=+3.2 \mu\text{atm}$ ) in November; 425.5  $\mu\text{atm}$  ( $\Delta f\text{CO}_2=+75.0 \mu\text{atm}$ ) in January/February, and 350.6  $\mu\text{atm}$  ( $\Delta f\text{CO}_2= -4.0 \mu\text{atm}$ ) in June for the latitudes south of 25.3°S. These results suggest that most of the atmospheric CO<sub>2</sub> penetrates in this oceanic area during wintertime. To the north of 25.3°S the surface seawater was a source of CO<sub>2</sub> for the atmosphere during all sampling seasons, and the continental shelf presented the highest  $\Delta f\text{CO}_2$ . The contribution of biological and temperature effects to the seasonal  $f\text{CO}_2(\text{sw})$  variations was calculated dividing the sampled region into three compartments: the continental shelf, the continental slope and the open ocean. Based on these calculations and that the data show a depletion of nutrients and chlorophyll-a during all seasons, it is suggested that the main contributions to the  $f\text{CO}_2(\text{sw})$  gradients in the open ocean and continental slope are the *in situ* temperature and the exchange of CO<sub>2</sub> with the atmosphere. In the shelf zone the vertical mixture processes must also be considered. The  $f\text{CO}_2(\text{sw})$  values change greatly from season to season, and these differences are extensive if taking into account the continental shelf and the continental slope, which present the highest supersaturation levels (up to 476.3  $\mu\text{atm}$ , 437.3  $\mu\text{atm}$  and 382.9  $\mu\text{atm}$ ) in summer, spring and winter, respectively. Data supports such as these, including ocean margins, can contribute on quantifying the oceanic uptake of atmospheric CO<sub>2</sub>.

### **High CO<sub>2</sub> fluxes from the air into a tidal flat area**

Wim Klaassen, Steven van Heuven and Henk de Groot  
Marine Biology, University of Groningen,  
P.O.Box 14, 9750 AA Haren, the Netherlands  
E-mail: W.Klaassen@biol.rug.nl

High CO<sub>2</sub> fluxes are common in coastal areas due to high input of nutrients and organic matter. It is, however, less clear whether a specific coastal area is a source or

a sink of CO<sub>2</sub>, as both the uptake for photosynthesis and the release by decomposition of organic matter can be quite high. Measurements of CO<sub>2</sub> fluxes from various types of coastal areas are recommended to quantify the impact of coastal seas on the global carbon budget. Here we present preliminary results of air-to-sea CO<sub>2</sub> exchange measured at the edge of the Wadden Sea, a midlatitudinal tidal flat area between the North Sea and the Netherlands. The fluxes were measured using the eddy-correlation method at a height of 50 m from a tower at the edge of the Wadden Sea in the period May to July 2003. The observed fluxes show a clear daily cycle of daytime CO<sub>2</sub> uptake and nighttime release. To our surprise, the magnitude of the fluxes was very high and comparable with fluxes from grasslands. The flux footprint of these measurements corresponds with the width (5 km) of the Wadden Sea. Smaller scale measurements of pCO<sub>2</sub> in the air and the water of a creek were taken as a first step to determine the CO<sub>2</sub> exchange in specific parts of the complex Wadden Sea ecosystem. Although we had expected that decomposition would dominate in this muddy area, a daytime uptake of CO<sub>2</sub> was found.

These preliminary findings show the Wadden Sea as an autotrophic area that absorbs high quantities of CO<sub>2</sub> in this time of the year. It is recommended to extend the measurement period in order to determine the annual CO<sub>2</sub> budget.

### **Interannual variability and future change of air-sea CO<sub>2</sub> fluxes in the Southern Ocean**

N. Metzl<sup>1</sup>, M. Bégovic<sup>1</sup>, E. Brévière<sup>1</sup>, C. Brunet<sup>1</sup>, A. Jabaud-Jan<sup>1</sup>, C.Lo Monaco<sup>1</sup>, C.Pierre<sup>2</sup>, A Poisson<sup>1</sup>, B.Schauer<sup>1</sup>, and B.Tilbrook<sup>3</sup>

<sup>1</sup>LBCM/IPSL, Université Pierre et Marie Curie, Case 134, 4 place Jussieu, 75252 Paris, France

<sup>2</sup>LODYC/IPSL, Université Pierre et Marie Curie, Case 100, 4 place Jussieu, 75252 Paris, France

<sup>3</sup>CSIRO, Div. Oceanography, Marine Lab., GPO Box 1538, Hobart, Tasmanie, 7001 Australia

E-mail: Metzl@ccr.jussieu.fr

The temporal variations of the carbon dioxide system, air-sea CO<sub>2</sub> fluxes and anthropogenic CO<sub>2</sub> in the ocean are analysed in the Southern Indian Ocean, based on historical and recent data collected in 1998-2003 during fifteen OISO and MINERVE cruises conducted onboard the R.V. Marion-Dufresne (IPEV/TAAF) and S.S. L'Astrolabe (IPEV/TAAF) in the frame of the long-term observational CARAUS program (INSU/IPSL). Seasonal, interannual and decadal variabilities of the carbon dioxide system will be presented. We also focus on rapid changes of ocean CO<sub>2</sub> sources and sinks associated with regional sea surface temperature anomalies; these changes are not only controlled by warming and cooling. For example during a warm event observed in summer 1998 in the open zone of the Southern Ocean, the oceanic CO<sub>2</sub> sink appears stronger (lower ocean fCO<sub>2</sub>) because the primary production dominates the temperature effect. Such signal was also observed in summer 2003. On the opposite, in austral summer 2002 we observed that the Southern Ocean was a CO<sub>2</sub> source, as large as the source observed during austral winter when the mixed layer is deep and primary production is low. Analysis of both rapid changes and slow trends of the carbon dioxide system in the ocean, in relation to external and internal

processes that operate during different situations (e.g., changes in light, cloud distributions, ocean stratification, primary production, ecosystems...), could help in evaluating future oceanic  $f\text{CO}_2/\text{DIC}/\text{TA}$  distributions and air-sea  $\text{CO}_2$  fluxes simulated by global coupled carbon models forced in climate change scenario.

### **New estimates of anthropogenic $\text{CO}_2$ in the Southern Ocean: Distribution and inventory along the WOCE I6 line**

C. Lo Monaco, N. Metzl, A. Poisson, C. Brunet and B. Schauer  
Laboratoire de Biogéochimie et Chimie Marines (LBCM/IPSL) - Université Pierre et Marie Curie - Paris, France  
E-mail: lomonaco@ccr.jussieu.fr

The Southern Ocean, where various water masses are formed (mode, intermediate, deep and bottom waters), has a high potential to absorb anthropogenic  $\text{CO}_2$  ( $C_{\text{ant}}$ ). However, most data-based and model estimates indicate low  $C_{\text{ant}}$  inventories south of  $50^\circ\text{S}$ . In order to investigate this paradox, we estimated the distribution of  $C_{\text{ant}}$  along the WOCE line I6 between South Africa and Antarctica (CIVA-2 cruise, 1996) by using a back-calculation technique previously applied to the North Atlantic Ocean (Körtzinger et al. in JGR 103, 1998). In the Subtropical/Subantarctic region ( $30\text{--}50^\circ\text{S}$ ), the formation and spreading of mode and intermediate waters result in a deep penetration of  $C_{\text{ant}}$  around  $40^\circ\text{S}$  (down to 1500-2000 m). Below the thermocline, uncontaminated cores of North Atlantic Deep Water overlies Antarctic Bottom Water (AABW) where low  $C_{\text{ant}}$  concentrations are detected. The distribution of  $C_{\text{ant}}$  we obtained in this region compares well with previous data-based and model estimates. South of the Polar Front ( $50^\circ\text{S}$ ), we estimated significant  $C_{\text{ant}}$  concentrations in Circumpolar Deep Water ( $>10\mu\text{mol}/\text{kg}$ ) and AABW ( $20\text{--}25\mu\text{mol}/\text{kg}$ ). Higher concentrations are detected along the continental shelf in AABW presumably formed on the eastern side of the section (e.g., Prydz Bay) compared to AABW of Weddell Sea origin. It is noted that, although transient tracers are not used in the back-calculation technique employed here, the distribution of  $C_{\text{ant}}$  is remarkably well correlated with CFCs. We re-evaluated the inventory of  $C_{\text{ant}}$  for the Southern Ocean and found higher values south of  $50^\circ\text{S}$  in the Antarctic zone ( $80\text{--}100\text{ mol}/\text{m}^2$ ) than north of  $50^\circ\text{S}$  in the Subtropical/Subantarctic zone ( $50\text{--}80\text{ mol}/\text{m}^2$ ). Our results confirm the role of Antarctic deep and bottom water formation as a sink for anthropogenic  $\text{CO}_2$ .

### **The role of the Mediterranean Overflow in the drawn-down of anthropogenic carbon**

Pérez, Fiz F., Alvarez, Marta, Shoosmith Deborah R., and Bryden, Harry  
Instituto Investigacions Mariñas (CSIC)  
c/Eduardo Cabello 6 VIGO E-36208 SPAIN  
E-mail: Fiz.perez@iim.csic.es

The high-salinity overflow from the Mediterranean sea, Mediterranean Overflow Water (MOW), mixes to depth with the surrounding water until the resultant mixed water reaches a stable level, at about 1200 meters depth. This new water mass is so

called Mediterranean Water (MW) with a salinity of 36.5 and potential temperature of 11.7°C. In this process an important entrainment of North Atlantic Central Water (NACW) is needed. From 3.5 Sv are dragged from the upper layer to finally yield a similar amount of MW. About 0.7 Sv of water of Atlantic origin is transformed into the Mediterranean Sea. The remainder is entrained when the MOW is spilled out from the Gibraltar Strait to be transformed into MW at about 1200 meter depth horizon in the North Atlantic.

The NACW is a water mass nearly saturated in anthropogenic carbon ( $C_{ANT}$ ) in about  $60 \mu\text{mol.kg-sw}^{-1}$ . The entrainment of NACW drives a sequestration of 0.075 Gt-C per year. This important amount represents about a quarter of the  $C_{ANT}$  driven by the Thermohaline Overturning Circulation (TOC) and is quite similar to the  $C_{ANT}$  transported by Labrador Sea Water. Additionally, recent evidence show that MOW has been becoming saltier over last four decades. New scenarios for the TOC suggest a slow down and a freshening of convective water masses in the North Atlantic. Although this implies a reduction in the natural sequestration of  $C_{ANT}$  by the TOC, smaller cells of upper water entrainment as the MW formation can increase the draw-down or compensate the TOC  $C_{ANT}$  sequestration and should be included and evaluated in future model scenarios.

We defined a box around the Strait of Gibraltar combining hydrographic and biogeochemical data from three 1998 hydrographic sections in the Eastern North Atlantic. The velocity field was carefully defined using an inverse box model conserving mass and minimizing the transport of deep water masses. The contribution of the different water masses was estimated by means of an Optimum Multi-Parameter (OMP) analysis and  $C_{ANT}$  was estimated according to Pérez et al. (DSRI, 49, 2002). We present the contribution of the different water masses in the Eastern North Atlantic to the transport of  $C_{ANT}$ , the main mechanisms involved in this transport and quantify the relevance of MW formation in the drawdown of  $C_{ANT}$ .

### **Zonal variability in carbon export and mesopelagic remineralization in the Southern Indian Ocean sector: Synthesis and global implications**

Pilskaln, Cynthia H.<sup>1</sup>, Trull, Thomas W.<sup>2</sup> and Treguer, Paul J.<sup>3</sup>

<sup>1</sup>Bigelow Laboratory for Ocean Sciences, 180 McKown Pt. Rd., West Boothbay Harbor, ME 04575 USA

<sup>2</sup>Antarctic CRC, University of Tasmania, GPO Box 252-80, Hobart, Tasmania 7001 Australia

<sup>3</sup>Institut Universitaire Européen de la Mer, UMR 6539, Technopole Brest-Iroise, Plouzane 29280, France

E-mail: cpilskaln@bigelow.org

Substantial international efforts over the past 10 years have been directed at quantifying carbon export dynamics in the Southern Indian Ocean and examining the role of this vast sector in Southern Ocean carbon cycling budgets. The research efforts include the Australian Subantarctic (SAZ) Program along 140° E, the French ANTARES/KERFIX Programs focused on the Subtropical Zone (STZ), the SAZ, and the Polar Frontal Zone (PFZ) in the Kerguelen Plateau region, the joint US-China-Australia program in the Antarctic Zone (AZ) near Prydz Bay, and the SOIREE Iron

Release Experiment. Results document major differences as well as some unexpected similarities between the circumpolar zones. For example: despite dramatically different plankton communities and seasonal nutrient dynamics, the SAZ deepwater export of POC is very similar to the PFZ but seasonal patterns vary. POC fluxes in the open-ocean AZ display strong interannual variability, associations with carbonate-bearing heterotrophs, and a lack of contribution from sea-ice algae. Additionally, the role of bacteria in the remineralization of sinking POC is much greater in the STZ compared to the PFZ, resulting in higher benthic carbon accumulation rates in the PZF. A synthesis of Southern Indian Ocean carbon export and remineralization data sets from  $\geq 1$  km is presented and compared to JGOFS Pacific and Atlantic sector data, with an emphasis on the efficiency of carbon remineralization in mesopelagic waters and its variability within the circumpolar zones of the Southern Ocean.

### **Enhanced open ocean storage of CO<sub>2</sub> from shelf sea pumping**

Helmuth Thomas, Yann Bozec, Khalid Elkalay, and Hein J.W. de Baar  
Royal Netherlands Institute for Sea Research (NIOZ), Department of Marine  
Chemistry and Geology, P.O. Box 59, NL-1790 AB Den Burg, Texel, The  
Netherlands  
E-mail: hthomas@nioz.nl

Coastal and marginal seas reveal strong biological activity, in part triggered by terrestrial and human impacts, and play an important role in the global carbon cycle by linking the terrestrial, oceanic and atmospheric carbon reservoirs. The high biological activity causes high CO<sub>2</sub> fluxes between the coastal and marginal seas and the atmosphere and the adjacent open oceans respectively. However, hitherto only limited information is available about these CO<sub>2</sub> fluxes. We present results of a carbon cycle study in the North Sea, which has been sampled for the first time ever as an entire marginal sea by 4 cruises covering all 4 seasons consecutively. The North Sea acts as a strong sink for atmospheric CO<sub>2</sub>, of which the largest part is exported to the North Atlantic Ocean, thus implying a highly efficient continental shelf pump. Globally, the uptake of CO<sub>2</sub> by coastal and marginal seas is approximately 20% of the world ocean's uptake of anthropogenic CO<sub>2</sub>.

## **TOPIC 7 Modelling Results**

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### **Upper ocean nutrient supply in a changing world**

S. Dutkiewicz, M. Follows and P. Parekh  
M.I.T., 54-1412, 77 Massachusetts Ave, Cambridge, MA 02139, USA  
E-mail: stephd@ocean.mit.edu

We use an ocean circulation, biogeochemistry and ecosystem model to explore the interactions between ocean circulation, productivity, nutrient limitation and



community structure. In particular, we explore the sensitivity of primary productivity in the ocean model to the aeolian iron supply, which may be modulated by anthropogenic climate forcing, human-induced desertification, or changes in surface ocean pH and solubility of dust. In a suite of sensitivity studies we find significant regional variations in response to an increase in the aeolian iron supply. Specifically, in a dustier world, the Southern Oceans exhibit higher productivity, there is a decrease in productivity throughout the Atlantic basin, and the Indo-Pacific basin has a regionally varying response: increased productivity in the upwelling regions, and decreased in the subtropical gyres.

These changes can be understood with the aid of a simple conceptual classification of the Southern and Indo-Pacific oceans into two regimes: (1) Upwelling, iron-limited, HNLC regions and (2) Macro-nutrient limited, oligotrophic subtropical gyres in which lateral Ekman transfer of nutrients from the surrounding upwelling regions is important for the long-term maintenance of production. Enhancing the aeolian iron supply to the upwelling regions relieves iron limitation and increases local primary and export production but reduces the lateral surface gradients and Ekman transfer to the neighbouring subtropical gyres. Consequently the gyres become further depleted in macro-nutrients and productivity decreases in response to global-scale iron fertilization.

We find that in the long term, Atlantic primary production is maintained by nutrients brought into the basin by the surface manifestation of the thermohaline circulation. A globally enhanced aeolian supply of iron leads to enhanced productivity in the Southern Ocean and Indo-Pacific upwelling regions, reducing the lateral transfer of macro-nutrients to the upper Atlantic and the basin as a whole is increasingly macro-nutrient stressed.

### **Biogeochemical cycles and ecosystem changes due to global warming obtained by 3-D ecosystem model**

Taketo Hashioka<sup>1</sup>, Yasuhiro Yamanaka<sup>2,1</sup>, and Maki N. Aita<sup>2</sup>

<sup>1</sup>Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan

<sup>2</sup>Frontier Research System for Global Change, Yokohama, 236-0001, Japan

E-mail: hashioka@ees.hokudai.ac.jp

To predict the effects of global warming on ecosystem dynamics and the effects of those changes in ecosystem dynamics on biogeochemical cycles, oceanic CO<sub>2</sub> uptake, and fishery resources, we need to develop coupled ecosystem-biogeochemical models that explicitly represent dynamics of oceanic circulation, phytoplankton, nutrients and fish. We have developed a global 3-D ecosystem-biogeochemical model, which extended from NEMURO (North Pacific Ecosystem Model Used for Regional Oceanography) of PICES (North Pacific Marine Science Organization), which has 15 compartments: two phytoplankton, three zooplankton, four nutrients, three particles, dissolved matter, total alkalinity, and total carbon. NEMURO has also been coupled with a fish bioenergetics and population model for two species of pelagic fish: Pacific Saury and Pacific Herring. Using data sets of observed climatology and simulated fields (COA-GCM developed by CCSR/NIES) as boundary conditions for our

ecosystem model, we conducted experiments for demonstrating the effects of global warming on ecosystems and pelagic fish.

The model results show increased vertical stratification in the subtropic-subarctic transition zone associated with global warming. As a result, in the transition zone, primary production and diatoms as a percentage of total phytoplankton drastically decrease at the end of 21<sup>st</sup> Century. Plankton species transition and temperature increase bring about a decrease in e-ratio (ratio of export production to primary production) and an increase in rain ratio (ratio of calcium carbonate to organic carbon in export production). These changes of biogeochemical cycles lead to feedback to future climate change.

The predicted knob length of adult Saury at the end of the 21<sup>st</sup> Century will be 30% smaller than at present. This is because the decrease in plankton concentration of the spring bloom in the transition zone leads to slow growth of Saury. The autumn horizontal migration by adult Saury shifted from the present route along the coast of Japan to the future offshore route will seriously impact Japanese fisheries.

Our model simulates important changes in fisheries as a result of global warming. This illustrates how modelling can also be useful for assessing impacts of global change on food supply.

### **Eddy-resolving modeling of anthropogenic tracer**

Akio Ishida<sup>1</sup>, Yoshikazu Sasai<sup>1</sup>, Yasuhiro Yamanaka<sup>1</sup>, and Hideharu Sasaki<sup>2</sup>

<sup>1</sup>Frontier Research System for Global Change

<sup>2</sup>Earth Simulator Center

E-mail: ishidaa@jamstec.go.jp

To improve our understanding of the processes determining the oceanic uptake and distribution of anthropogenic CO<sub>2</sub>, we have developed high-resolution ocean general circulation models (OGCMs). Chlorofluorocarbon (CFC) is known as an ideal tracer for evaluating the ability of OGCMs to simulate the uptake and redistribution of anthropogenic CO<sub>2</sub> in the oceans. The distributions of CFC simulated with two OGCMs are compared with the observed data at some sections to validate the model results and to investigate the effects of mesoscale motions on the tracer distributions. One of the models is the OFES (OGCM on the Earth Simulator) which has 1/10 degree horizontal grid spacing and can resolve explicitly mesoscale eddies. Another is the OGCM with 1/4 degree which is called eddy-permitting or marginally eddy-resolving model. Both models simulate the characteristic distribution of CFC in the ocean such as the bowl-shaped distribution associated with the thermocline structure in subtropics. One of the remarkable differences is in the Southern Ocean, where deep penetration is simulated in the OFES which reproduces more realistic newly formed deep water than in the 1/4 degree model. Another improvement is in the lower thermocline and the intermediate layer in the northwestern North Pacific and in the South Indian Ocean. The comparison of isopycnal distributions shows that more CFC spreads equatorward from the Subarctic and Subantarctic regions in the OFES.

## **A re-evaluation of the $\Delta C^*$ method to estimate anthropogenic carbon in the ocean**

Katsumi Matsumoto<sup>1</sup> and Nicolas Gruber<sup>2</sup>

<sup>1</sup>Geological Survey of Japan, AIST, Tsukuba, Ibaraki, 305-8567, Japan

<sup>2</sup>IGPP & Dept. of Atmospheric Sciences, UCLA, CA 90095, USA

E-mail: katsumi@ni.aist.go.jp

Anthropogenic carbon in the ocean is not directly measurable. It is instead estimated by removing the large natural or background component from the measured dissolved inorganic carbon concentrations. The separation of the tiny anthropogenic component involves a number of assumptions and a series of calculations using various nutrient and gas measurements, which are collectively called the  $\Delta C^*$  method. In recent studies (*Sabine et al.*, *Global Biogeochemical Cycles* 16, 10.1029/2001GB001639, 2002; *Sabine et al.*, *Global Biogeochemical Cycles* 13, 179-198, 1999), this method has been applied to tracer data from the recently completed World Ocean Circulation Experiment and basin-wide estimates of anthropogenic carbon in the Indian and Pacific Ocean have been obtained for the first time.

Here we evaluate the  $\Delta C^*$  method using a set of synthetic (model) “data”. If the  $\Delta C^*$  method is accurate, the “data”-estimated anthropogenic carbon should be consistent with that simulated directly by the model. We find however that the “data”-estimated anthropogenic carbon tend to overestimate the simulated, suggesting perhaps systematic biases in the method. We discuss some of the possible reasons.

## **Estimates of air-sea anthropogenic carbon dioxide flux from ocean interior carbon measurements and Ocean General Circulation Models**

Sara Mikaloff Fletcher<sup>1</sup>, Nicolas P. Gruber<sup>1</sup>, Andrew R. Jacobson<sup>2</sup>, Manuel Gloor<sup>2</sup>, Jorge Sarmiento<sup>2</sup>, and the Ocean Inversion Project Modellers

<sup>1</sup>The University of California, Los Angeles, 5839 Schlichter Hall, Los Angeles, CA 90095-1567

<sup>2</sup>Program in Atmospheric and Oceanic Sciences, Sayre Hall, Forrestal Campus, Princeton University, PO Box CN710 Princeton, NJ 08544-0710

E-mail: fletcher@igpp.ucla.edu

The exchange of anthropogenic carbon dioxide across the air-sea interface cannot be measured directly; however, the concentration of anthropogenic carbon in the ocean can be determined from DIC and nutrient data. Using a recently developed inversion technique, global and regional air-sea fluxes of anthropogenic carbon dioxide have been estimated using the resulting distribution of anthropogenic carbon, an *a priori* estimate of the spatial pattern of the carbon flux, and pathways and rates of ocean transport and mixing given by an Ocean General Circulation Model (OGCM). Previous sensitivity studies have shown that model circulation is one of the most important sources of error in the ocean inversion. We present estimates of anthropogenic carbon exchange using a suite of six different OGCMs in order to quantify the robustness of our results and explore the role of different representations of ocean circulation in the inversion.

The inverse model estimates a global anthropogenic carbon uptake of 2.0 to 2.3 Pg C/yr for a nominal year of 1995. The greatest anthropogenic carbon uptake occurs at mid- to high latitudes, with a large anthropogenic carbon sink in the Southern Ocean, while the bulk of the anthropogenic carbon storage occurs at mid-latitudes. The regional carbon flux estimates are most robust for northern mid-latitude regions. The estimates are the most uncertain for high-latitude regions, especially the Southern Ocean. Preliminary results suggest that for most regions, inverse estimates of anthropogenic carbon flux based on different OGCMs are in better agreement than estimates using forward simulations of the same models.

### **Sensitivity of air-sea CO<sub>2</sub> exchange to the organic matter flux in a 3D Earth system model**

A. Mouchet<sup>1</sup> and E. Driesschaert<sup>2</sup>

<sup>1</sup>Université de Liège, Département d'astrophysique, de géophysique et d'océanographie, Allée du 6 août, 17, B-4000 Liège, Belgium

<sup>2</sup>Université Catholique de Louvain, Institut d'astronomie et de géophysique Georges Lemaitre, Chemin du cyclotron, 2, B-1348 Louvain-la-Neuve, Belgium

E-mail: A.Mouchet@ulg.ac.be

The ocean biological pump is a key process in controlling atmospheric CO<sub>2</sub> levels. Though not directly affected by CO<sub>2</sub> partial pressure it is, however, strongly sensitive to any change in the ocean circulation.

Modifications in the nutrient supply rate to the upper layers may impact the biological pump either by directly affecting the export production magnitude or by leading to a change in species composition.

In the latter case the amount of organic carbon leaving the euphotic layer might remain the same while reaching different depths, a redistribution which would affect air-sea carbon fluxes.

Recent global analyses of sediment trap data revealed that the flux of organic carbon to the deep ocean is strongly enhanced by the presence of mineral ballast (Armstrong et al., 2002; François et al., 2002). It seems that CaCO<sub>3</sub> shells are much more efficient in transferring organic carbon to the deep ocean than opal skeletons (Klaas and Archer, 2002). Modelling studies show a significant sensitivity of the atmospheric CO<sub>2</sub> toward the remineralization depth of organic matter.

In order to address the potential feedbacks from the ocean biology on climate we use a global model of the Earth system (LOVECLIM). This model is made up of a comprehensive model of the oceanic carbon cycle (LOCH), a coarse-resolution three-dimensional atmosphere—sea-ice—ocean model (ECBILT-CLIO) and a dynamical model of the continental biosphere (VECODE). The simplified atmospheric component results in a low computational cost, hence allowing for a number of experiments to be performed over several centuries.

In a series of sensitivity studies we examine the impact of rising atmospheric CO<sub>2</sub> on the oceanic carbon uptake and we analyze the relative strengths of the various

contributions (physical / biological). Experiments in which the organic matter vertical distribution varies with ecosystem composition are also performed.

### **Aragonite undersaturation in the surface Southern Ocean by 2100**

J. Orr, L. Bopp, O. Aumont, R. Key, C. Sabine, G.-K. Plattner, F. Joos, E. Maier-Reimer, M.-F. Weirig, R. Schlitzer, R. Matear, R. Slater, J. Sarmiento, S. Doney, K. Lindsay, M. Follows, A. Yool, A. Mouchet, Y. Yamanaka, and A. Ishida  
\*LSCE/CEA Saclay, Bat. 709 L'Orme, F91191 Gif-sur-Yvette, France  
E-mail: orr@cea.fr

At present, the lowest surface carbonate ion concentration [ $\text{CO}_3^{2-}$ ] in the world ocean is found in the Southern Ocean (i.e., all ocean south of  $60^\circ\text{S}$ ). Previous studies of potential future changes in calcification by marine organisms have focused on other regions where corals (aragonite) and coccolithophorids (calcite) are abundant. Yet the Southern Ocean is far from being devoid of marine calcifiers. For example, the pteropod *Limacina helicina* is known as an abundant primary consumer and a major food source for fishes and whales in the Ross Sea. Here we have estimated the Southern Ocean decline in [ $\text{CO}_3^{2-}$ ] that will occur over the next 100 years due to increases in atmospheric  $\text{CO}_2$  and its invasion into the ocean. We have compared two atmospheric  $\text{CO}_2$  scenarios: the continually increasing IPCC IS92a scenario (788 ppmv in 2100) and the IPCC S650 stabilization scenario (563 ppmv in 2100). As a starting point, our calculations rely on observed DIC and alkalinity, measured during WOCE and JGOFS. These have recently been summarized in a new global gridded data product (Glodap). To that reference, we added simulated perturbations in DIC due to the invasion of anthropogenic  $\text{CO}_2$  into the ocean. Alkalinity was assumed to remain constant. To provide uncertainties, we used DIC perturbations simulated by the 13 global ocean models that participated in the second phase of Ocean Carbon-Cycle Comparison Project (OCMIP-2). At present, the Southern Ocean's surface [ $\text{CO}_3^{2-}$ ] averages  $110 \mu\text{mol kg}^{-1}$ , based on the Glodap Alkalinity and DIC. This is already  $19 \mu\text{mol kg}^{-1}$  lower than during preindustrial time, based on data-based estimates of anthropogenic DIC. In year 2100 under scenario IS92a, Southern Ocean surface [ $\text{CO}_3^{2-}$ ] declines to an unprecedented level,  $57 \pm 5 \mu\text{mol kg}^{-1}$  (OCMIP-2 median  $\pm$  range/2). The simultaneous decline of [ $\text{CO}_3^{2-}$ ] in subsurface waters, causes the Southern Ocean's aragonite saturation horizon (ASH, where  $\Omega_{\text{arag}} = 1$ ) to shoal from its present average depth (875 m) all the way up to the surface. In the second scenario atmospheric  $\text{CO}_2$  is stabilized at 650 ppmv, surface waters in the Southern Ocean remained slightly supersaturated ( $\Omega_{\text{arag}} = 1.1$ ), except in the Weddell Sea; waters deeper than 50 m were undersaturated. To our knowledge, no studies are available to indicate how such undersaturation would affect the life cycle and abundance aragonitic organisms. In summary, our results indicate that present unabated rise in atmospheric  $\text{CO}_2$  will lead to a dangerous decline in Southern Ocean [ $\text{CO}_3^{2-}$ ] by the end of the century. This could in turn cause a major shift in ecosystem structure.

## **Testing a 1D coupled physical-biogeochemical model in eco-regions of the ocean for predicting the response to the increased atmospheric CO<sub>2</sub> over the last decade**

B. Pasquer<sup>1</sup>, G. Laruelle<sup>3</sup>, N. Gypens<sup>1</sup>, H. Goose<sup>2</sup>, and C. Lancelot<sup>1</sup>

<sup>1</sup>Université Libre de Bruxelles, Ecologie des Systèmes Aquatiques. Campus Plaine, bvd du Triomphe.CP 221, 1050 Bruxelles, Belgium

<sup>2</sup>Institut d'Astronomie et de Géophysique Georges Lemaître, Université Catholique de Louvain

<sup>3</sup>Department of Earth Sciences – Geochemistry. Faculty of Geosciences Utrecht University P.O. Box 80.0213508 TA Utrecht, The Netherlands

E-mail: bpasquer@ulb.ac.be

We present results obtained with the SWAMCO model, a complex model of the marine planktonic system calculating C, N, P, Si, Fe cycling within the upper ocean, the export production and the exchange of CO<sub>2</sub> between the ocean and atmosphere. The model, constrained by chemical (Fe, P, Si, N), physical (light, temperature, salinity) and biological (grazing) controls, explicitly details four relevant phytoplankton functional groups with respect to C, N, P, Si, Fe cycling and climate change. Those are diatoms, nano- and picoplankton, Coccolithophoridae, and *Phaeocystis* sp. whose growth regulation by light, temperature and nutrients has been obtained based on a comprehensive analysis of literature reviews on these taxonomic groups. The performance of SWAMCO is evaluated in a 1D physical frame throughout its cross application in eco-regions with contrasted key species dominance, export production, CO<sub>2</sub> air-sea fluxes and where biogeochemical time-series data are available for model initialisation and results comparison. These are: (i) the ice-free Southern Ocean Time Series station KERFIX (50°40S, 68°E) for the period 1993-1994; (ii) the sea-ice associated Ross Sea domain (76°S, 180°W) of the Antarctic Environment and Southern Ocean Process Study AESOPS in 1996-1997; and (iii) the North Atlantic Bloom Experiment NABE (60°N, 20°W) in 1991. We then explore the ocean response to increased atmospheric CO<sub>2</sub> by running SWAMCO scenarios over the last decade.

### **Ocean biology in a high-CO<sub>2</sub> world**

P. Schultz, R.D. Slater, A.R. Jacobson, and J.L. Sarmiento

Program in Atmospheric and Oceanic Sciences, Sayre Hall, Princeton University,

P.O. Box CN710, Princeton, NJ 08544, USA

E-mail: pschultz@princeton.edu

Modeling changes in ocean primary production (PP) in response to global warming is crucial for understanding the role of the oceans in climate. Biological activity and thus uptake of CO<sub>2</sub> by phytoplankton is dependent on oceanic temperature, stratification, circulation, convective overturning, cloud cover and sea ice extent. Coupled climate models predict dramatic changes in these parameters. We apply an empirical model of ocean biology (Sarmiento et al., submitted), which relates changes in the physical ocean-atmosphere system to changes in ocean biology, to a climate warming simulation. In our warming scenario atmospheric greenhouse gas concentrations

increase at 1% per year until reaching four times the initial concentrations after 140 years and are held constant thereafter until the end of the simulation in 2290.

High biological productivity is usually associated with upwelling velocities or strong vertical mixing whereas downwelling and permanently stratified regions are characterized by low productivity. Therefore, Sarmiento et al. (submitted) use the sign of the vertical velocity at 50 m depth, wintertime maximum mixed layer depth, and sea ice cover to divide the world into six biomes. Global warming leads to a contraction of the seasonal sea ice biome by 70% in the northern hemisphere and 27% in the southern hemisphere, whereas the subpolar upwelling biome expands by 47% in the northern hemisphere and 17% in the southern hemisphere.

Downwelling biomes only expand by 2.4% globally, but the pattern is heterogeneous with the strongest increases occurring in the Southern Hemisphere where a general southward shift of the fronts can be observed. Sarmiento et al. (submitted) use a multivariate linear regression of satellite ocean color against climatological observations to constrain an empirical model of chlorophyll. Our simulation suggests significant changes in chlorophyll concentrations. Three features stand out in the response to global warming: (1) large increases in most of the Southern Ocean and the South Atlantic, (2) decreases in coastal and equatorial upwelling biomes, and (3) decreases in the North Atlantic and the North Pacific in response to the retreat of the seasonal sea ice biome.

To estimate the response of ocean PP to global warming we use three different algorithms, which relate changes in PP to predicted changes in chlorophyll concentrations, temperature, and light supply. Predictions from the three algorithms range from increases in globally integrated PP of 9.8% at the low end to 26.7% at the high end. More work is needed to resolve this discrepancy.

### **Modeling the global ocean ecosystem to predict the ocean storage of CO<sub>2</sub>**

Akio Sohma<sup>1</sup>, Tadahide Kakio<sup>1</sup>, Yasuyuki Sekiguchi<sup>1</sup>, Jun Hirosaki<sup>1</sup>, and Makoto Akai<sup>2</sup>

<sup>1</sup>Fuji Research Institute Corp (FRIC) 2-3 Kanda-Nishikicho, Chiyoda-ku, Tokyo 101-8443, Japan

<sup>2</sup>National Institute of Advanced Industrial Science and Technology (AIST) 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564 Japan

E-mail: sohman@cyg.fuji-ric.co.jp

A global ocean ecosystem model, "DONGRI", including simplified air system was developed. The purposes of the model are (1) to understand the physical and biochemical processes/interactions in ocean system or among air and ocean system and (2) to predict the effects of anthropogenic CO<sub>2</sub> or purposeful CO<sub>2</sub> enrichment to/from ocean considering not only physical, but also biochemical processes in long-term scale. DONGRI can represent the dynamics of 20 model components: Total CO<sub>2</sub>, Phyto-Plankton, Zoo-Plankton, Particulate non-living Organic Matter, Dissolved Organic Matter, CaCO<sub>3</sub>, Dissolved Oxygen, NO<sub>3</sub>-N, NH<sub>4</sub>-N, N<sub>2</sub>, PO<sub>4</sub>-P, Ca, Total Alkalinity, pH, pCO<sub>2</sub>, etc. and the interactions/relationships among compartments. Though this model description (option 1) could present the biogeochemical

autonomous reaction to the environmental impacts concerned with CO<sub>2</sub>, many subjects of observation are needed for model calculation and verification. Thus, the model has also another treated option (option 2) which calculates the total TCO<sub>2</sub> production/consumption caused by biochemical processes analytically but not represent the model components (not consider the autonomous reaction to the CO<sub>2</sub> impacts). The physical transport was from the outputs of the ocean global circulation model. In this stage, the model was applied to the global ocean divided into 9 regions in horizontal (Arctic, North Atlantic, South Atlantic, Antarctic-A, North Pacific, South Pacific, Antarctic-P, Indian, and Antarctic-I) and 35 layers in vertical, and the air system was presented as one box. Option 1 is selected in the north pacific region and other regions applied option 2. The calculated period was from year 1800A.D. to year 7000A.D. Though modeling the many biogeochemical interactions, model outputs reproduced the observed data well on most compartments and flux value.

From the sensitive analysis of the model, we indicated the contribution of biochemical processes for the prediction of CO<sub>2</sub> storage in air and ocean. In addition, we predicted the effects of CO<sub>2</sub> ocean sequestration on ocean and air, and defined the efficiency of sequestration as "CO<sub>2</sub> in air without sequestration" minus "CO<sub>2</sub> in air with sequestration" over "mass of CO<sub>2</sub> sequestration". From the results, the efficiency of sequestration rapidly decreases during early times from injection regardless of injection depth/area because pCO<sub>2</sub> decrease in air caused by sequestration decreases CO<sub>2</sub> absorption (CO<sub>2</sub> flux from air to sea) on sea surface. This result indicates that the efficiency of all of the CO<sub>2</sub> control technique for air, such as geological sequestration, also has the possibility to rapidly decrease by including the ocean effects.

### **Global and regional changes to calcification rate in a high-CO<sub>2</sub> ocean**

Ian J. Totterdell

Met Office Hadley Centre for Climate Prediction and Research, Fitzroy Road, Exeter, EX1 3PB, U.K.

E-mail: Ian.J.Totterdell@soc.soton.ac.uk

Laboratory studies (e.g., Riebesell et al., Nature, v407, pp364-367, 2000) have shown that the rates of calcification in the coccolithophores *Emiliana huxleyi* and *Gephyrocapsa oceanica* depend on the carbon system in seawater. In particular, the invasion of CO<sub>2</sub> from the atmosphere leads to a reduction in the rate in both species. Given current and projected future anthropogenic emissions of CO<sub>2</sub> this result has implications for the survival of coccolithophores, for the strength of the carbonate pump and for the uptake of anthropogenic CO<sub>2</sub> by the ocean. The Hadley Centre Ocean Carbon Cycle (HadOCC) model (Palmer and Totterdell, Deep-Sea Research I, v48, p1169-1198, 2001) has been adapted to examine these changes on global and basin scales. Following spin-up under a pre-industrial atmosphere, the model was run for a historical/future simulation from 1860 to 2094. Five different carbon tracers were used, all affected identically by organic biological production and respiration. The first tracer was also affected by carbonate precipitation and dissolution that was independent of the state of the carbon system (the default for the HadOCC model). For the four extra tracers the carbonate formation rate varied according to the carbonate saturation state or the concentration of H<sub>2</sub>CO<sub>3</sub>, using the relationships identified by Riebesell et al. for the two species. The results show a significant effect



on global carbonate formation by the end of the simulation: in the tracers using the *G. oceanica* relationship the anthropogenic CO<sub>2</sub> causes a 31% reduction using the carbonate saturation state or a 44% reduction with the H<sub>2</sub>CO<sub>3</sub> concentration. In the latter case there are locations in the Arctic Ocean where carbonate formation no longer occurs. The tracers using the *E. huxleyi* relationship show a smaller effect, with reductions of 10% and 18% respectively, and no areas have ceased to allow formation. The effects vary regionally, and that variation is different depending on whether H<sub>2</sub>CO<sub>3</sub> concentration or saturation state is used. In terms of the ocean cycle, however, the changes are small: in 2094 the ocean uptake of anthropogenic CO<sub>2</sub> is no more than 0.12 Pg C/yr (or 3%) greater for the tracers with variable carbonate formation, and the inventory is 9 Pg C (2%) greater. So while this study shows that changes in ecosystem structure will possibly be significant, changes to the ocean carbon cycle may be less important.

### **New 3-D modelling for evaluation of CO<sub>2</sub> ocean sequestration**

Yasuhiro Yamanaka<sup>1,3</sup>, Yoshio Masuda<sup>2</sup>, Taketo Hashioka<sup>3</sup>, Michimasa Magi<sup>2</sup>, and Takashi Ohsumi<sup>2</sup>

<sup>1</sup>Frontier Research System for Global Change, Yokohama, 236-0001, Japan

<sup>2</sup>Research Institute of Innovative Technology for the Earth, Kyoto, 619-0292, Japan

<sup>3</sup>Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan

E-mail: galapen@jamstec.go.jp

CO<sub>2</sub> ocean sequestration is regarded as one of mitigating climate change due to anthropogenic emissions of CO<sub>2</sub>, which is to be discussed in the “IPCC special report on CO<sub>2</sub> capture and storage” issued in the next year. To investigate impacts of injected CO<sub>2</sub> on marine ecosystems, we need new models for investigating where injected CO<sub>2</sub> moves and how it is diluted during a few weeks through a few years, which are exactly equivalent to classical concepts, advection and diffusion of water masses, in physical oceanography. Therefore, we use an eddy-permitting model with a Lagrangian tracer method, to avoid an artificial diffusion in numerical problem with an Eulerian passive tracer used in the previous studies.

We used CCSR Ocean Component Model developed in University of Tokyo and applied to the western North Pacific (115°E-180°E, 10°N-60°N). The model has horizontal resolution of 1/4 by 1/4 degrees and 54 layers with realistic bathymetry. The forcing data are based on monthly mean OMIP data. Velocities of Lagrangian tracers are calculated from the discretized velocities in the OGCM with an interpolation method satisfying mass conservation (Masuda and Ikeda, *Submitted to JTECH*), which is a development from Döös (1995) and Blanke and Raynaud (1997).

The model successfully simulates the realistic circulation. The Kuroshio separates from the Japan coast and turns east at 37°N. The Lagrangian tracers injected in the southern region of Japan (129°E-130°E, 25°N-26°N, and 780m-1200m depth) are squeezed to line-form advected by the lower branch of Kuroshio current and are divided into some parts by mesoscale eddy activity. That is, CO<sub>2</sub> concentrations of the particles are rapidly diluted due to eddy activity. To evaluate our Lagrangian method, we also calculated an Eulerian tracer with two advection schemes: upstream

difference (first-order accuracy) and Quickest (third-order accuracy). Although performance of Quickest scheme is much better than upstream's, concentration calculated by the Eulerian tracer with Quickest rapidly decreases, which shows less realistic dilution than that calculated by the Lagrangian tracers.

We clearly demonstrated that a Lagrangian method combined with a high resolution OGCM is a powerful tool for assessing CO<sub>2</sub> injection to marine environment.

## TOPIC 8

### **Organizations, Programs, or Scientific Activities related to scientific or technical aspects of ocean carbon science**

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#### **The Centre for observations of Air-Sea Interactions and Fluxes (CASIX)**

N.J. Hardman-Mountford, Prof. J. Aiken, & the CASIX team  
Plymouth Marine Laboratory, Prospect Place, Plymouth PL1 3DH, UK  
E-mail: casix\_dir@pml.ac.uk

The Centre for observations of Air-Sea Interactions and Fluxes (CASIX) is a UK NERC Centre of Excellence in Earth Observation. The purpose of CASIX is to exploit new-generation Earth Observation (EO) data to advance the science of air-sea interactions and reduce the errors in the prediction of climate change. The primary goal is to quantify accurately the global air-sea fluxes of CO<sub>2</sub> using state-of-the-art, error-budgeted models. New sensors in new satellites (Terra, Envisat, Aqua) combined with established sensors, give high-precision, high-resolution data of atmosphere, ocean surface layer properties and ocean biogeochemical variables daily, globally, and long term. By using and assimilating EO data in coupled physical-ecosystem models CASIX can achieve its goals. CASIX combines the Met Office ocean modelling team and UK academic research groups, with Space Agency support, to accelerate the development of methods of forecasting Earth system processes.

#### **CLIVAR's contribution to the Global Carbon Project : Cross-project Ocean Carbon activities**

K.L. Hill<sup>1</sup>, M. Hood<sup>2</sup>, C. Sabine<sup>3</sup>, R.A. Feely<sup>3</sup>, K. Lee<sup>4</sup>, B. Tilbrook<sup>5</sup>, A. Koertzinger<sup>6</sup>

<sup>1</sup>CLIVAR IPO, Southampton Oceanography Centre, United Kingdom.

<sup>2</sup>International Oceanographic Commission, UNESCO, Paris.

<sup>3</sup>NOAA PMEL, Seattle, USA.

<sup>4</sup>Pohang University of Science and Technology, Pohang, Republic of Korea.

<sup>5</sup>CSIRO and Antarctic Climate and Ecosystems CRC, Hobart, Australia.

<sup>6</sup>Institut für Meereskunde, Kiel, Germany

E-mail: klh@soc.soton.ac.uk

The World Climate Research Programme's (WCRP) Climate Variability and Predictability Project (CLIVAR) focuses on three scientific streams:

**GOALS (Global Ocean Atmosphere Land System):** A study of seasonal-to-interannual climate variability and predictability of the global ocean-atmosphere-land system

**DecCen (Decadal to Centennial Climate Variability):** A study of decadal-to-centennial climate variability and predictability

**ACC (Anthropogenic Climate Change):** modelling and detection of anthropogenic climate change.

The ACC stream undertakes to:

- Develop understanding, modelling and predictive capabilities of the response of the climate system to the anthropogenic increases in radiatively active gases and changes in aerosols
- Identify the patterns of anthropogenic modification to the mean state and to the variability of the climate system
- Use the understanding of natural climate variability derived from the other two CLIVAR component programmes as a baseline for detecting the trends and signatures associated with increases in greenhouse gases and the effects of other anthropogenic changes.

Clarifying the ocean's role in the global carbon cycle, the variability in the system and how this is modified by anthropogenic CO<sub>2</sub> enrichment is of central importance to fulfilling CLIVAR's aims in this area. This will also form CLIVAR's contributions to the Global Carbon Project. To address this CLIVAR will be working with 3 key collaborators:

- International Ocean Carbon Coordination Project (IOCCP)
- Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) project
- Surface Ocean - Lower Atmosphere Study (SOLAS)

Building on the observations collected through the WOCE/JGOFS partnership, CLIVAR and IOCCP are working together to ensure that both hydrographic and carbon observation requirements are addressed in the CLIVAR/CO<sub>2</sub> Repeat Hydrography cruise planning. To facilitate the coordination of research in important cross-cutting issues, each of the CLIVAR Basin panels have a carbon representative; a full member who represents the IOCCP and IMBER projects to foster efforts in areas of common interest. To address air-sea flux issues, CLIVAR will be working closely with SOLAS by planning cross-cutting projects.

This poster will outline examples of cross-cutting issues and early implementation results.