Final Report

Direct Ocean Sequestration Experts' Workshop

U.S. Dept. of Energy
National Energy Technology Laboratory

Held at

Monterey Bay Aquarium Research Institute (MBARI)

Moss Landing, CA 95039

Feb. 27- March 1, 2001

EXECUTIVE SUMMARY

This workshop is one critical outcome of a major planning activity within the U.S. Department of Energy, and the publication of a significant "road mapping" document on carbon sequestration (www.ornl.gov/carbon_sequestration/). Chapter 3 of that report deals specifically with ocean CO_2 sequestration. The strategic road mapping exercise provided essential leadership in setting major directions, but gave few tactical details on research priorities and timelines for evaluating and achieving an effective national capability. That is a function of this report.

In practice we already have an ocean fossil fuel CO_2 disposal program of massive proportions. Surface ocean CO_2 disposal, that is uptake from the atmosphere by gas exchange with surface ocean waters, is now about 25 million tons of CO_2 per day. Until very recently this has been regarded as a great boon to mankind, in permitting growth of fossil fuel use to aid our economy, and ameliorating concerns over possible climate change. However the pH of surface ocean waters has, in spite of the chemical buffering provided by ocean alkalinity, already changed globally by about 0.1 pH units since the beginning of the industrial revolution. And, if "Business as Usual" continues throughout this century, not only may we expect the probability of substantial climate change, but also the certainty that the pH of surface ocean waters will decline to levels that may exert enormous stress on coral reefs world wide.

The problem is that on contemporary time scales we are using only a very small fraction of oceanic capacity: the relatively thin surface layer. The rate of ocean deep water formation (or the removal rate of surface ocean waters) is sufficiently slow that it will take thousands of years to achieve this. The mean ventilation age of deep ocean waters is close to 550 years.

The question of whether it is wise, or possible, or effective, to limit the atmospheric disposal/surface ocean uptake step, with its attendant global warming, and inject CO_2 directly into the deep ocean, thus holding climate change and surface ocean acidity to "acceptable" levels has long been debated. Although direct ocean CO_2 sequestration was first proposed over 25 years ago, and many theoretical analyses have been published, it is only in the last 5 years that experimental techniques permitting true small-scale field observations have evolved.

From the DoE road map, and from other published work, a fairly clear sense of the quantities required for climate control has emerged. For example, if a target of stabilization of atmospheric CO_2 levels at about 550 ppm (about twice pre-industrial values) is set, then deviations from present trends of about 3.7 billion tons CO_2 per year by 2025, and 14.6 billion tons per year by 2050 will be required. Should some other target be set, then scaling laws will apply. This may be achieved by a combination of conservation/efficiency, fuel substitution, and geologic/ocean CO_2 sequestration.

These quantities present an enormous challenge to society. Each option has its advocates, and major policy choices have yet to be made. However if equal weight is given then the global sequestration target may approach 1.2 billion tons CO_2 per year by 2025. An advantage of sequestration is that it makes enhanced use of most of the trillion dollar fossil fuel infrastructure and workforce that we depend on to create wealth, and provide power for our technologically advanced society, until such time as new power systems emerge.

The U.S. share of this target is likely to be about 25%, or 0.3 billion tons per year. This could encompass both geologic (land based) and oceanic options, based upon plant siting, economic choices, environmental policy etc. If the ocean option is taken as 25% of this, then we would consider 75 million tons CO_2 per year (or 0.2 million tons per day). Note that this impressive number is less than 1% of even present day global surface ocean uptake, which will itself increase substantially as atmospheric CO_2 levels rise.

It is well recognized that the vast alkaline chemical capacity of the ocean will, over many centuries, absorb up to 85% of all fossil fuel CO_2 emissions to the atmosphere. The volume of ocean water is 1.37×10^{21} liters; it has an alkalinity of 2.3 mmol/liter. So large is this capacity that some 4,500 billion tons of CO_2 could be accommodated with a pH change of about 0.3. This is approximately equal to the change that will be experienced by surface waters at doubling of atmospheric CO_2 levels. In practice quantities an order of magnitude less than this would be possible or advisable – and only if carefully defined cost, safety, and environmental concerns can be met.

The purpose of this Experts' workshop was to present new results, and to plan important new opportunities, for research in this rapidly emerging field. The goal is to provide the fundamental science base for developing a significant national ocean carbon sequestration capability within the next decade.

This workshop consisted of 19 invited presentations, and 3 targeted working groups that met to define R&D priorities, identify potential research participants and their capabilities, and develop a timeline for basic science and controlled field experiments. The result was a consensus on critical needs in the science of CO_2 chemistry associated with disposal technologies; on oceanic mixing processes in dispersing the material and its entrainment in the global ocean circulation; and on essential biological studies for assessing the environmental impact. In making these assessments the group was keenly aware of the trade off in balancing costs and concerns over localized deep ocean intervention, versus the emerging impacts of global climate change and ocean surface biology and chemistry worldwide.

Each working group provided a set of priorities and timelines for research.

The working group on Physical Chemistry dealt with the complex problems of transport and injection of a CO_2 stream into the deep ocean. The greatest uncertainty is associated with the formation of the icelike CO_2 clathrate hydrate. While formation is possible at depths exceeding about 350 m, reliable predictions of hydrate formation, stability and impact are not presently possible. Current hydrodynamic models cannot explicitly include hydrate effects due to this lack of important information. Additional uncertainties can also be caused by the presence of impurities in the CO_2 stream, some of which can form mixed hydrates with the CO_2. Formation of hydrate in transportation lines and delivery systems is also a potential problem. Other important issues concern the reaction of CO_2, and any impurities, with the materials used to pump, transport and deliver the CO_2 stream. Understanding the impacts on the ocean and sediment chemistry is also important. The Physical Chemistry group proposed 14 initiatives to address these issues that could lead to significant accomplishments over an eight-year period. Most of this work would involve laboratory and small-scale field testing; however, the use of appropriate large-scale experiments and natural laboratory sites were also recommended to provide end-point model validation and address broad, multi-disciplinary issues associated with direct oceanic sequestration.

The working group on Ocean Physics defined the critical enabling research necessary for reliable assessment of biological impacts and sequestration efficiency. Physical measurements and models essential to understanding the fate of a CO_2 plume were considered. For the near field, studies of plume dynamics are critical; at intermediate scales, enhanced mixing due to tidal interactions with local topography will dominate. For the far field, the use of ocean general circulation models (OGCM) to evaluate Antarctic emergence and long term fate of the signal were reviewed. Micro-scale mixing, autonomous vehicle, and float technologies for physical observations will be required. Modeling challenges include improving grid resolution to account for eddies, boundary currents, convection, and topography and developing methodologies to improve the cost effectiveness for much longer simulations. A key area related to defining sequestration efficiency is understanding the dynamics associated with Southern Ocean ventilation. The possibilities for collaboration were reviewed and suggestions for key experiments made. Key research initiatives were identified and cast into an an eight-year research plan.

Biological studies to assess the environmental acceptability of deep ocean disposal are essential. For the near field studies of the microbial drivers of the fundamental biogeochemical cycles in marine sediments will be required. On a larger scale the deep ocean possesses natural pH gradients of about 0.3 pH units between the North Atlantic, and North Pacific end members. Yet the Atlantic and Indo-Pacific animal populations differ. Many marine animals migrate daily from intermediate depths to the surface through large natural vertical pH gradients; many others do not. Animals uniquely adapted to deep sea niches have limited physiological capacity for pH buffering.
These studies will help define acceptable ranges for pH and CO_2 perturbations, and this will drive the design of deep ocean release technologies.

WORKSHOP AGENDA

Tuesday, February 27

OPENING

7:30 – 8:30 a.m. Registration and Continental Breakfast

8:30 – 8:45 a.m. Welcome and Opening Remarks
Julie Packard
Monterey Bay Aquarium

8:45 – 9:00 a.m. Introductory Remarks
Perry Bergman
U.S. Department of Energy, National Energy Technology Laboratory

THE ISSUES
State of the Science and Technology

9:00 – 9:20 a.m. IEA Workshops
John Davison
IEA Greenhouse Gas R&D Programme

9:20 – 9:40 a.m. U.S. Perspective
Eric Adams
Massachusetts Institute of Technology

9:40 – 10:00 a.m. Japan’s Perspective
Takashi Ohsumi
Research Institute of Innovative Technology for the Earth (RITE)

10:00 – 10:20 a.m. Norway’s Perspective
Guttorm Alendal
Nansen Environmental and Remote Sensing Center

10:20 – 10:40 a.m. Break

SUMMARY OF CURRENT EFFORTS
Active Ocean Sequestration Research Efforts

10:40 – 11:00 a.m. International Field Experiment
Stephen Masutani
University of Hawaii

11:00 – 11:20 a.m. MBARI Experiments and emerging technologies
Peter Brewer

	Monterey Bay Aquarium Research Institute
11:20 – 11:40 a.m.	Japan’s Current Work Izuo Aya Ship Research Institute
11:40 – 12:00 p.m.	Norway’s Current Work Guttorm Alendal Nansen Environmental and Remote Sensing Center
12:00 – 1:00 p.m.	**Group Lunch**
1:00 – 1:20 p.m.	McDermott Technology, Inc. Hamid Sarv
1:20 – 1:40 p.m.	DoE Center for Research on Ocean Carbon Sequestration (DOCS) Ken Caldeira Lawrence Livermore and Lawrence Berkeley National Labs.
1:40 – 2:00 p.m.	National Energy Technology Laboratory Robert Warzinski
	Ocean Science Capabilities
2:00 – 2:15 p.m.	Tracking a rising stream of CO_2 bubbles and droplets Gregor Rehder, MBARI
2:15 – 2:30 p.m.	Large Scale Deliberate Tracer Experiments Ray Schmitt, Woods Hole Oceanographic Institution
2:30 – 2:45 p.m.	**Break**
2:45 – 3:00 p.m.	Floats and the Deep Circulation Russ Davis, Scripps Institute of Oceanography
3:00 – 3:15 p.m.	Naval Research Laboratory Interests Richard Coffin, Naval Research Laboratory
3:15 – 3:30 p.m.	International Experiment Technical Committee Report C.S. Wong, Institute of Ocean Sciences
3:30 – 3:45 p.m.	Mineral Geochemistry and CO_2 Sequestration Klaus Lackner, Los Alamos National Laboratory
3:45 – 4:15 p.m.	AUVs and Tracking a CO_2 Release James Bellingham, Monterey Bay Aquarium Research Institute
4:15 – 4:45 p.m.	Deep Ocean Biology and CO_2 James Barry, Monterey Bay Aquarium Research Institute

4:45 – 5:00 p.m. Review and discussion

5:00 – 6:30 p.m. Reception – hosted by MBARI

Wednesday, February 28

WHAT NEEDS TO BE DONE

7:30 – 8:30 a.m. Continental Breakfast

8:30 – 8:40 a.m. Opening Remarks
Peter Brewer, Monterey Bay Aquarium Research Institute

8:40 – 9:40 a.m. Chemistry/Physics

E. Dendy Sloan	Colorado School of Mines
Izuo Aya	Ship Research Institute
Russ Davis	Scripps Institution

9:40 – 10:40 a.m. Biology

Craig Young	Harbor Branch Oceanographic Institute
Jun Kita	Marine Ecological Research Institute
James Barry	Monterey Bay Aquarium Research Institute

10:40 – 11:00 a.m. Break

11:00 – 12:00 p.m. Modeling

Ken Caldeira	Lawrence Livermore National Laboratory
Guttorm Alendal	Nansen Environmental and Remote Sensing Center
James Orr	LSCE, CEA Saclay

12:00 – 1:00 p.m. Group Lunch

1:00 – 1:15 p.m. Introduction of Breakout Groups
Peter Brewer Monterey Bay Aquarium Research Institute

1:15 – 4:30 Breakout Groups Meet
Physical Chemistry - E. Dendy Sloan
Ocean Physics – Russ Davis
Biology - Craig Young and James Barry
Modeling - Ken Caldeira and James Orr

4:30 – 5:00 p.m. Breakout Groups Interim Report

5:00 p.m. Adjourn for the day

Thursday, March 1

	WRAP UP AND ASSIGNMENTS
7:30 – 8:30 a.m.	Continental Breakfast
8:30 – 8:40 a.m.	Opening Remarks Peter Brewer, Monterey Bay Aquarium Research Institute
	Reporting of Breakout Groups
8:40 – 9:00 a.m.	Physical Chemistry, E. Dendy Sloan, Colorado School of Mines
9:00 – 9:20 a.m.	Ocean Physics, Russ Davis, Scripps Institution of Oceanography
9:20 – 9:40 a.m.	Ocean Biology, Craig Young, Harbor Branch Oceanographic Institute
9:40 – 10:00 a.m.	Ocean Modeling, Ken Caldeira, Lawrence Livermore National Laboratory
10:00 – 10:15 a.m.	Teams and Writing Assignments Peter Brewer, Monterey Bay Aquarium Research Institute
10:15 – 10:30 a.m.	Break
10:30 – 12:00 p.m.	MBARI Tour and Technology Demonstration
12:00 – 1:00 p.m.	Group Lunch
1:00 – 1:30 p.m.	Closing Comments Peter Brewer Monterey Bay Aquarium Research Institute Robert Warzinski U.S. Department of Energy - National Energy Technology Laboratory
1:30 p.m.	**Adjourn** (Report writing assignees will be asked to stay)

EXPERT PRESENTATIONS

SUMMARY

About 47 attendees heard 20 expert presentations. This was followed by discussion, and by the convening of 3 Working Groups on Physical Chemistry, Ocean Physics, and Ocean Biology. The Working Group reports are appended here.

The group first heard (Bergman) a retrospective on past projections of fuel costs, and costs of pollutant mitigation strategies. It was clear that both were grossly overestimated, and that unforeseen improvements in technology and economics had had major impact. The message was clear – that great progress is likely in carbon sequestration technologies. Presentations on current programs - international, U.S., Japan, and Norway followed Davison, Adams, Ohsumi, and Alendal). Here the focus has been on planning, and modeling, with significant field studies yet to come about. However small scale (1-10 liter) field experiments using ROV systems for CO_2 delivery and observation have now been accomplished (Brewer), and they yield powerful results with clear demonstration of hydrate formation. These results are complemented by high pressure laboratory experiments in Japan (Aya), and in the U.S. (Warzinski).

Regional numerical modeling of large-scale release of CO_2 at intermediate depth off the coast of Norway was described (Alendal), with well-resolved plume dynamics. Results from global modeling of large-scale releases of CO_2 at various ocean depths were presented (Caldeira). Here the consistent feature is of Antarctic emergence, and the details of this were described. Pipeline technologies for large-scale deep-sea CO_2 delivery are essential, and the critical engineering design and deployment features were presented (Sarv).

Components of these studies can now be tested experimentally in the field. The dissolution rate of a rising CO_2 plume within the hydrate phase space has been measured (Rehder), and the results of large (basin, decadal) scale deliberate tracer (SF_6) releases were presented (Schmitt). Results from probing of the deep ocean circulation by very large numbers of floats were described (Davis).

There are also many aspects of this problem that remain untested. Possible issues in oceanic microbiology were discussed (Coffin). The advances made in geologic sequestration, and conversion of CO_2 into solid mineral forms were presented (Lackner), and questions over sediment interactions were raised and discussed. Questions over the ability to measure the behavior of a large CO_2 plume in real time were raised, and remarkable advances in AUV technology and pH mapping were presented (Bellingham, Ryan).

Questions over the biological impacts of large scale CO_2 injection were reviewed (Barry). These would occupy much of the subsequent discussion. Large localized pH/CO_2 changes in the immediate vicinity of a release are to be expected, much as in the release from a smokestack plume to the air today. However the residual far field effects drew most attention. Many mid-water marine animals migrate vertically through large (0.3-0.5) natural pH gradients daily, and thus may not be stressed. But animals adapted to residence in the low oxygen – low pH zone have minimal pH buffering capacity.

ABSTRACTS OF PRESENTATIONS

Introduction to Carbon Sequestration

Perry Bergman
U. S. Dept. of Energy, National Energy Technology Laboratory
Pittsburgh

Perry Bergman presented a review of the overall status of US CO_2 sequestration efforts. He noted that the greatest cost of the process is that of capture, but that great advances were being made. He cited a recent reduction in costs of a factor of 4, and noted that when SOx and NOx removal was first mandated there were predictions of dire economic consequences. Yet today these costs have dropped dramatically. He noted that the carbon tax of $50 ton CO_2 in Norway had made possible the Sleipner project. And that today the US is sending 500 tons of CO_2 per day to the Weyburn field in Saskatchewan for oil field flooding and sequestration.

The DoE Fossil Energy sequestration budget today is about $18.8M, and with the Office of Science support, and private cost sharing, some $50M in projects is now underway. He closed by noting that we were not good at predicting future energy costs. At the time of the 1973 oil crisis industry specialists were asked to predict future oil costs 30 years out. The results were uniformly high by a factor of 3 compared to today's market costs. The message is that the ingenuity of mankind in technology, and the efficiency of markets, can have tremendous impact in reducing costs, and that we should be very optimistic about the future of making the world a better place.

The International Energy Agency Workshops

John Davison
IEA Greenhouse Gas R&D Programme
Cheltenham, England

The International Energy Agency Greenhouse Gas R&D programme (IEA GHG) is funded by some 16 member countries plus 6 major industrial companies. IEA GHG is broadly interested in ways of reducing the imapct of energy use on climate, and recognizes the size and importance of the present day oceanic sink. Possible direct ocean disposal has long been considered. John Davison reported on the results of 4 technical workshops held in 1995-96, and 3 recent stakeholder forums, each of 30-60 people, held in London, New York, and Kyoto. The purpose of these forums was to "identify the questions stakeholders would like to see addressed to begin to establish whether ocean storage of CO_2 is a robust environmental management strategy."

The result of these meetings was agreement that reductions in fossil fuel use would be preferred over use and disposal, that all techniques should be evaluated on a common basis, and efficiency of sequestration, were major concerns. For oceanic disposal the issues of biological impacts in both the near and far fields were addressed. It was noted that the acceptable level of risk, as for any new technology, would attract the attention of society as a whole. At the treaty level, the London Convention now generally prohibits disposal from ships, except for certain materials specified in the Convention. One of the most memorable quotes came from a young Japanese student at the Kyoto workshop: “Global warming won’t wait for us. Proceed with caution, and be brave enough to stop if necessary.”

U.S. Perspective on Carbon Sequestration Planning

Eric Adams

Mass. Inst. Technol.

Eric Adams presented the history and current status of almost 12 years of MIT involvement in ocean carbon sequestration planning and modeling. It has been known for a long time that the ocean sink is enormous, but questions on details remain. The proposed technologies are mostly proven, but not well documented in this application. There are many disposal scenarios, but as yet no single choice. And there are issues of scale and public perception.

For physico-chemical processes the scale ranges from <1cm droplet/hydrate studies, to plume modeling of 1 – 100m scale, to regional modeling at >10 km scale. Outreach to groups in Norway and Japan for modeling has been useful and productive. Work on pH/biological studies has been of laboratory scale. He noted that issues of scale are particularly important for plume/biology issues, but that public perception of such large-scale studies remains a problem. Current efforts are in modeling sinking plumes and interfacing plume models with global ocean models.

Laboratory and model studies must ultimately be complemented by field studies. Several years ago a three-phase plan was suggested:
Phase I: Plume physics and chemistry: 0.1-1 kg/sec for 1 week, representing a single nozzle injector.
Phase II: Biological impact studies: 0.1 – 1 kg/sec for 1 year.
Phase III: Full-scale demonstration: 100 kg/sec for 1 year at a 500MW plant location.

The Perspective in Japan on Carbon Sequestration

Takashi Ohsumi

Res. Inst. Innovative Technol. Earth

Japan

Japan has been involved in ocean carbon sequestration studies for about 12 years, with Mitsubishi, SRI, and CRIEPI being sponsoring organizations, and establishing laboratories for high pressure work. Takashi Ohsumi reported on history and progress. The finding in 1989 of natural liquid CO_2 seeps on the sea floor by Sakai and colleagues stimulated further original work, including the imaging of a block of solid CO_2 carried down by a manned submersible. A primary experimental site of 5,800m depth, 1000 km south of Tokyo, has been selected for study. Planned research includes physical circulation at the site, mapping of the CFC tracer field for water mass ventilation ages, and collection of natural zooplankton populations for pH sensitivity studies. The work is cooperative with droplet/hydrate laboratory studies. He noted that although Japan’s energy use per GDP unit was only about one third of US usage CO_2 sequestration was nonetheless a serious national issue, and that he welcomed cooperative programs.

Norway's Perspective on Carbon Sequestration
Guttorm Alendal
Nansen Environmental Remote Sensing Centre

Guttorm Alendal reported on the results of 10 years of CO_2 sequestration science in Norway, mostly as modeling studies. Fossil fuel extraction and use represents the biggest industry in Norway, and thus there are national concerns about increasing atmospheric disposal. With Norway geologic sequestration is preferred, and the offshore oil and gas infrastructure (rigs, pipes, wells) supports this activity. He noted that the proximity of Norway to locations of North Atlantic deep water formation favored oceanic retention of disposed CO_2. The results of modeling the injection of 200,000 – 800,000 tons CO_2/yr at Haltenbanken were presented. Key findings were the need to inject well below winter time mixed layer depths, with 925m depth selected as giving excellent retention. Both local/regional, and global circulation models were used. International comparisons of sub-models for plume characteristics were made with groups in Japan, and discrepancies in CO_2 droplet drag coefficients, and dissolution rates, were found. These have now been resolved, and very good agreement reached. The need now is for realistic meso-scale field experiments to test these results, and to formally incorporate biological studies and questions surrounding hydrate formation.

Planned International Field Experiment
Stephen Masutani
Univ. Hawaii

The International Field Experiment had its origins at the IPCC COP 3 meeting in Kyoto, at which time a co-operative agreement to carry out research on ocean CO_2 sequestration was signed by government representatives from the US, Japan, and Norway. Soon after the group received additional participation with representatives from Canada, ABB (Switzerland), Australia, and CRIEPI (Japan). Stephen Masutani brought the meeting up to date on plans and progress.

The location chosen was off Kona, Hawaii, and plans were to use an existing pipeline to inject several tons of liquid CO_2 at about 800m ocean depth, at varying release rates to test models of dispersal and plume dynamics. Biological studies were not initially planned since the impacts are expected to be so small and temporary that it would not be a practical or appropriate experimental design for adequate research. However local citizen opposition revealed a degree of fear and skepticism, and plans for the Hawaii site were changed.

The revised plan is to use a ship/ROV, and barge, combination at another location. The barge is to transport the CO_2, and dispense it through a flexible pipe to the sea floor at 800-1000m depth. An ROV is to latch onto the dispensing nozzle array to image the release rate and droplet characteristics. A submersible is to sample the mid water field for chemical variables. Moorings are to provide the physical background. Flow rates of 0.1-1 kg/sec are considered, with 40-60 tons released over 10-14 days.

Small Scale Deep Sea Experiments and Emerging Technologies
Peter Brewer
MBARI

For about 5 years the research group at MBARI have been carrying out small scale (0.5-7 liter) experiments, using MBARI's ROVs for precise delivery of liquid CO_2 at depths from 350-

3600m, for fundamental chemical, physical, and biological studies. Peter Brewer described recent progress with a focus on depths below 3000m, where liquid CO_2 is denser than sea water, and the experiments are gravitationally stable.

The neutrally buoyant depth was determined by direct observation of a floating 2cm diameter droplet. The equations of state give good approximations, but the formation of a hydrate film, and the absorption of water into the CO_2 mass, add complexity. The result was 2710m (2712 dbars) for waters off Northern California: below this depth liquid CO_2 will sink. Liquid CO_2 deposited into a beaker at 3000m depth did not produce the overflow effect from large volume changes observed in an earlier experiment at 3600m depth. It simply slowly dissolved. Liquid CO_2 deposited into a 20 inch diameter corral on the sea floor was left for time dependent study. The estimated lifetime was a few days. Major questions remain about the behavior and fate of a solid mass of hydrate, as opposed to a liquid mass covered with a thin (monomolecular) hydrate skin. Brewer reported on a very and recent and challenging experiment carried out at 1032m depth in collaboration with USGS, and LLNL colleagues. Here laboratory synthesized CO_2 hydrates were transported to the sea floor, and their fate imaged with a high resolution camera. Dissolution of a cylindrical mass approximately 3cm by 1 cm occurred in about 8 hours. Precise reporting of the rates is to follow.

Laboratory Studies in Japan

Izuo Aya
Ship Research Institute
Osaka, Japan

Izuo Aya presented a review of the various ocean disposal technologies actively being considered in Japan:

1. The "J-pipe" technique proposed by Saito, in which a N_2-CO_2 gas mixture is introduced, and the CO_2 preferentially dissolved and piped to depth (Fig.1).
2. Injection of cold (-55 degrees) CO_2 to form a sinking mass.
3. Creation of a >6000m deep CO_2 lake, where the liquid is more dense than the hydrate.
4. Injection of CO_2 to from a hydrate beneath the sea floor.
5. Creation of a CO_2 lake at about 3500m depth, where dense CO_2 saturated water in the boundary layer inhibits convection and increases lifetime.
6. Formation of a hydrate slurry at about 500m depth in disposal pipe for transport to >3500m (Fig. 2).

This latter method has been tested on a small scale in a joint SRI-MBARI experiment using the ROV Ventana. A mass of liquid/solid CO_2 at –55 degrees was released at 500m depth, and imaged as it sank, and then rose (and dissolved) as it warmed. These important rate data provide the first field test of the fate of CO_2 released at tanker transport temperatures. From these data it can be calculated that a 40 cm diameter mass containing 50% dry ice released at 100m will sink to >3500m depth, thus providing effective sequestration.

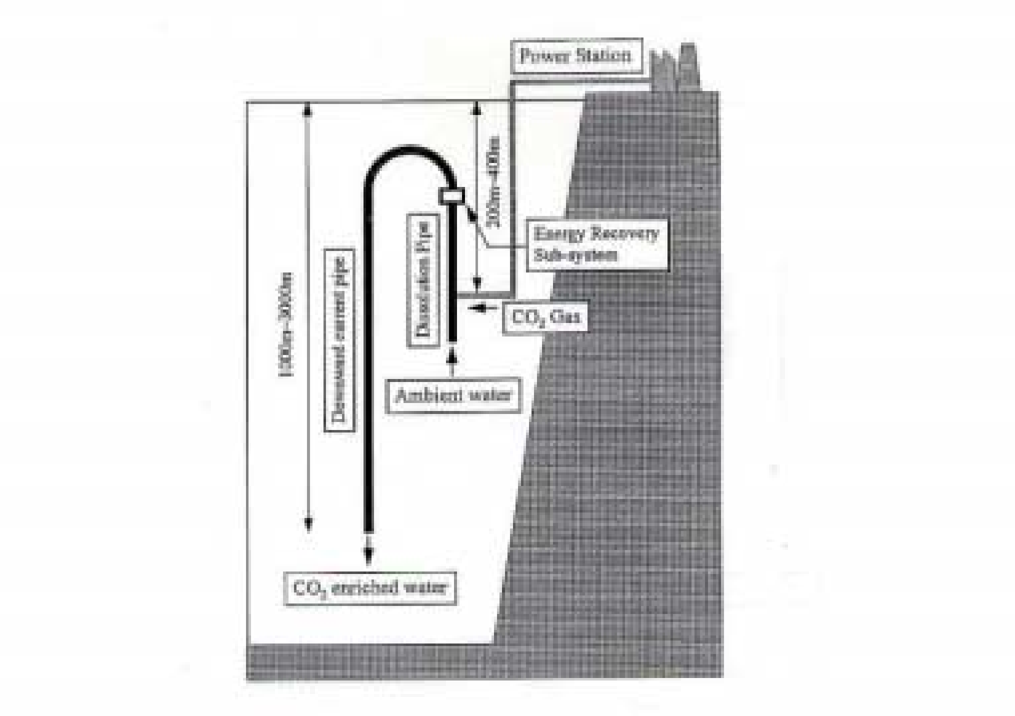


Figure 1. Concept of J-pipe disposal with sea water solubility based separation of a N_2-CO_2 mixture, followed by release of excess N_2, and downward flow of dense CO_2 saturated sea water.

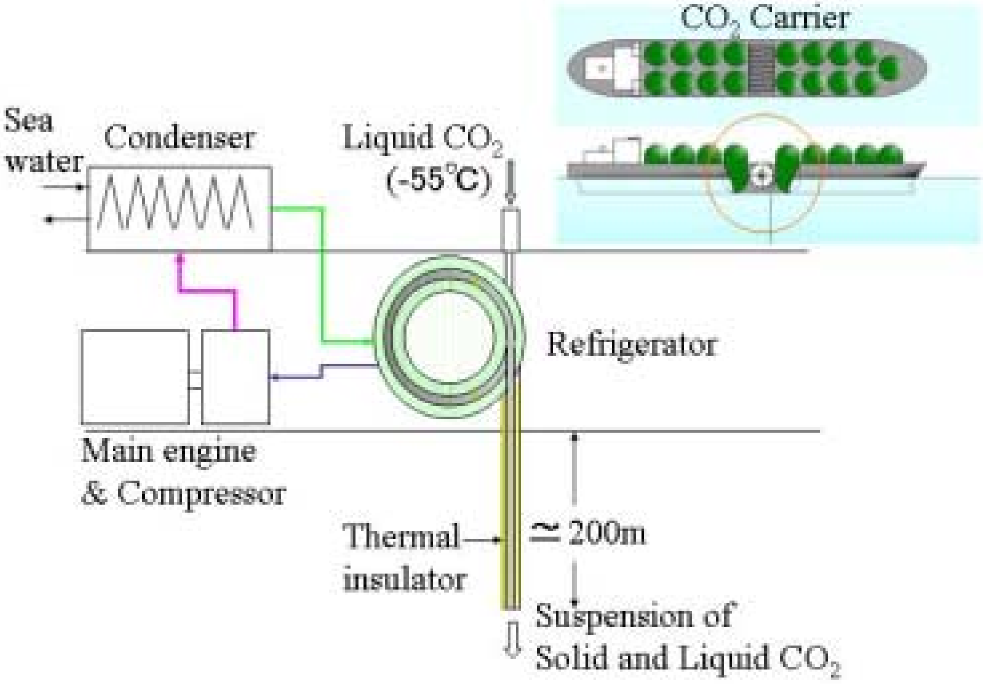


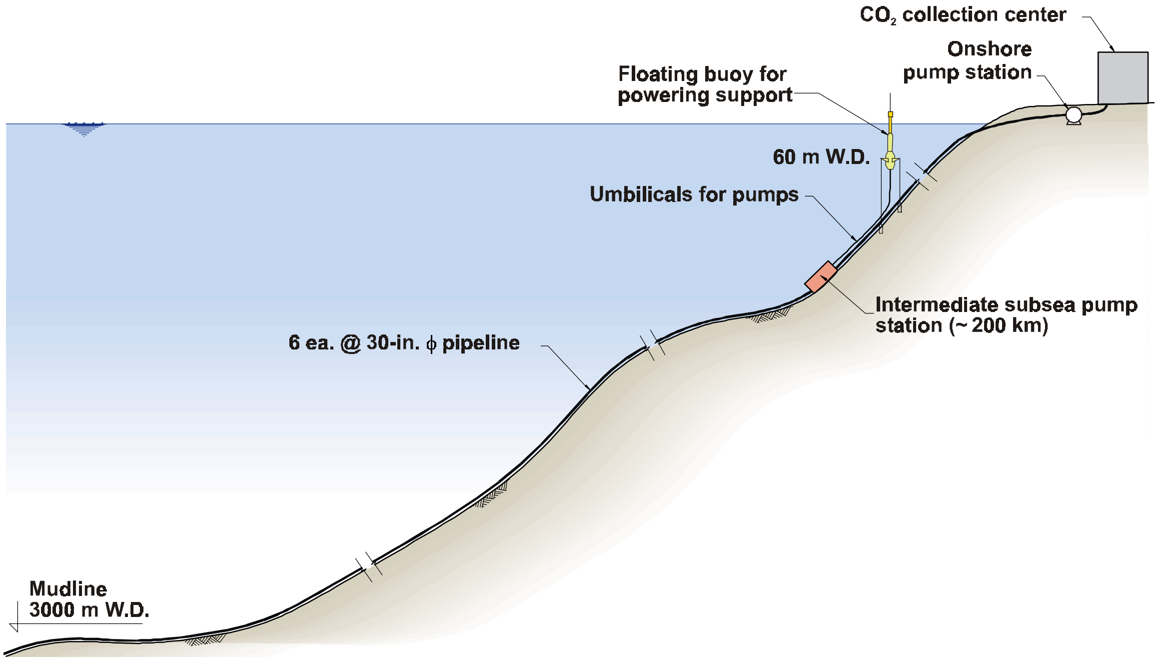
Figure 2. Concept of tanker based CO_2 disposal as a dense slurry of cold CO_2 and hydrate.

Deep Sea CO_2 Pipeline Technologies

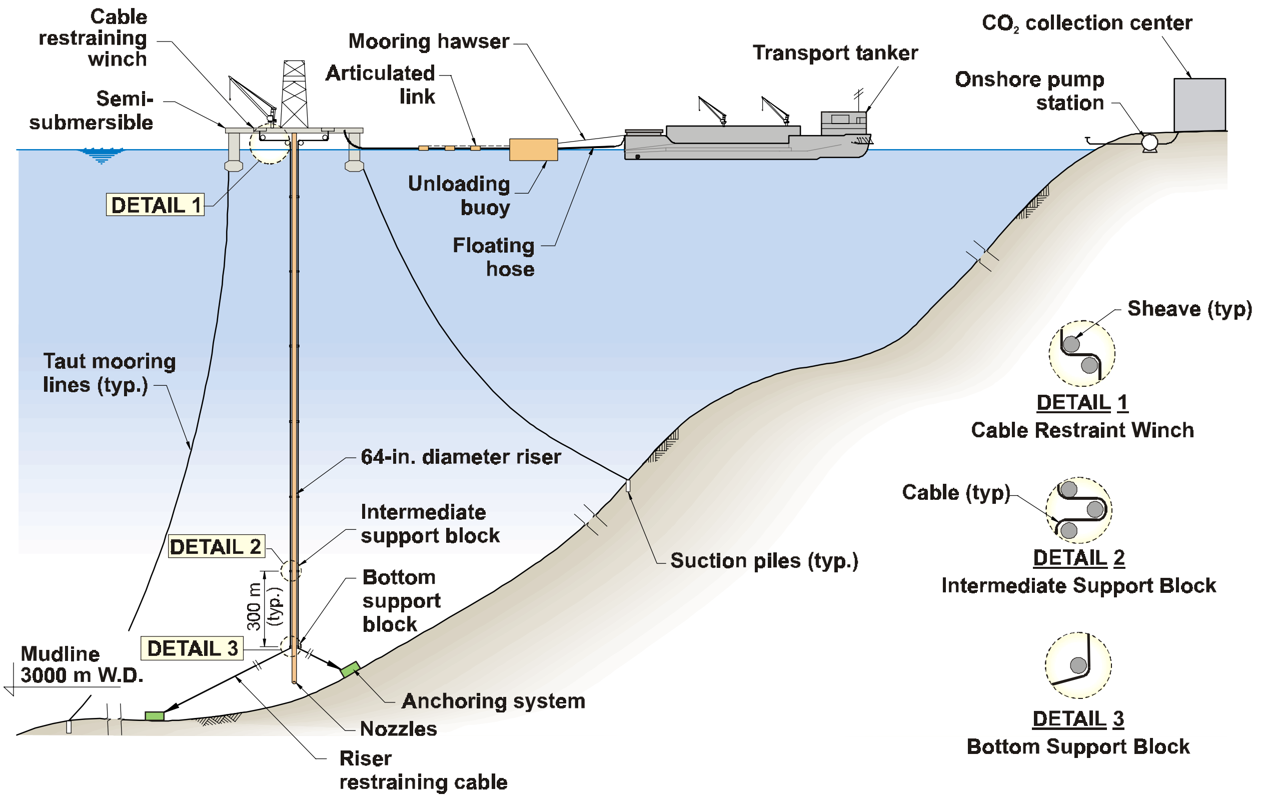
Hamid Sarv

McDermott Technology, Inc.

Pipeline technologies are critically involved in all aspects of CO_2 sequestration. Hamid Sarv reviewed the present state of knowledge and essential design criteria. The study here was to evaluate the technology for transport and storing very large quantities (200×10^6 tons/year) of CO_2 in the deep ocean. Both vertical (ship deployed) and sea floor pipes were examined. Both S-lay and J-lay deployment designs were reviewed, with 3000m of 64 inch diameter pipe of 1.25 inch wall thickness being selected for the pipe. Models of stress anticipated during deployment were presented, as were early studies of the corrosion protection around the injection nozzle. The preliminary cost estimates were favorable with the pipeline costs being <$2/ton CO_2 stored.



Sub-sea pipeline CO_2 transport option



CO_2 tanker transport option

DoE Center for Research on Ocean Carbon Sequestration
Ken Caldeira
LLNL-LBL

Ken Caldeira reviewed 3 topics:

1. The formation of a DoE Ocean Carbon Sequestration Center at both Lawrence-Livermore and Lawrence Berkeley Laboratories to coordinate research in the chemical, physical, and biological areas of research.

2. The results of global modeling of simulated CO_2 injections at several ocean depths down to 3000m. The model has 1°x1° resolution, and runs simulating release of 0.1 GtC/yr for 100 years were shown, with model runs extending 1000 years (see Figure 1 below). In general there is a strong correlation between ocean retention and depth of injection. For a 1000m release there is leakage back to the atmosphere after several decades before eventual ocean re-absorption. For the 3000m release scenario the main thermocline acts as an effective barrier to upward transport outside the southern polar latitudes, and eventual Antarctic emergence is seen. For 3000m releases overall ocean retention of about 90% is seen over 1000 years, with less than 10% atmospheric leakage on intermediate time scales.

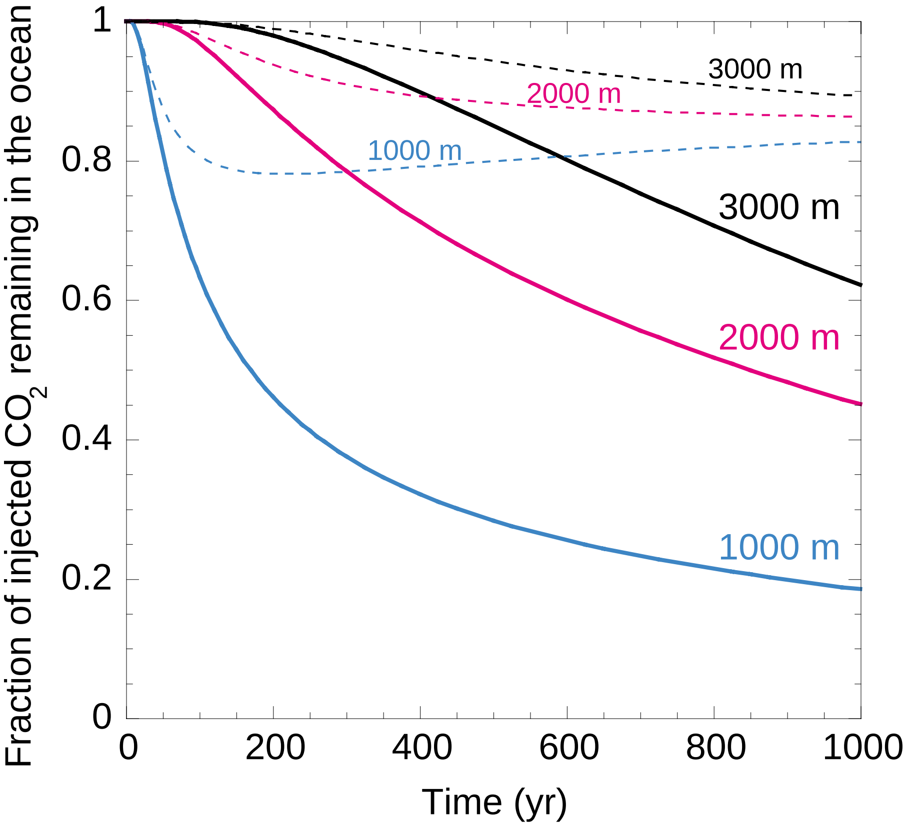


Figure 1. Simulation results for sequestration effectiveness for injections at 1000m, 2000m, and 3000m (Caldeira et al., 2001). Dashed lines show the fraction of carbon remaining in the ocean that has not degassed to the atmosphere and been re-absorbed by the ocean.

3. Studies of the neutralization of CO_2 by reaction with crushed $CaCO_3$ rock were carried out. This permits shallow ocean disposal without creating large pH gradients, and increases ocean alkalinity. The benefits could be substantial, but the tradeoffs of increased costs for mining transport and crushing, plus a very large water demand, need careful evaluation. Lab. reactor studies are proceeding.

Progress at the National Energy Technology Laboratory

Robert Warzinski
NETL
Pittsburgh

Laboratory simulations of CO_2 disposal processes are critical, and the dynamic processes are the most difficult to simulate. Robert Warzinski reviewed progress with water tunnel technology at NETL. Experiments began in 1993 with a low-pressure tunnel that was designed with flow elements that created a velocity well in which a rising bubble could be poised against an opposing downward water flow. A video tape of an elegant experiment was shown, in which an air bubble was balanced in the downward flow. A high-pressure system designed to simulate ocean depths down to 3400 m has been constructed. Figure 1 shows a view of this unit, which consists of two windowed viewing sections (foreground) and a flow loop. The inset shows a CO_2 drop stabilized in the system. Basic bubble dynamics theory was reviewed, and it was shown that the presence of a hydrate film should affect the dynamical wobbles characteristic in the size range etc. considered.

The studies are complemented by more conventional pressure vessel experiments in which single phase CO_2 hydrate formation from cooling saturated fluids was demonstrated. Once hydrate nucleation occurs then a bubble (~ 1cm diameter) is covered with a hydrate skin in about 1 second.

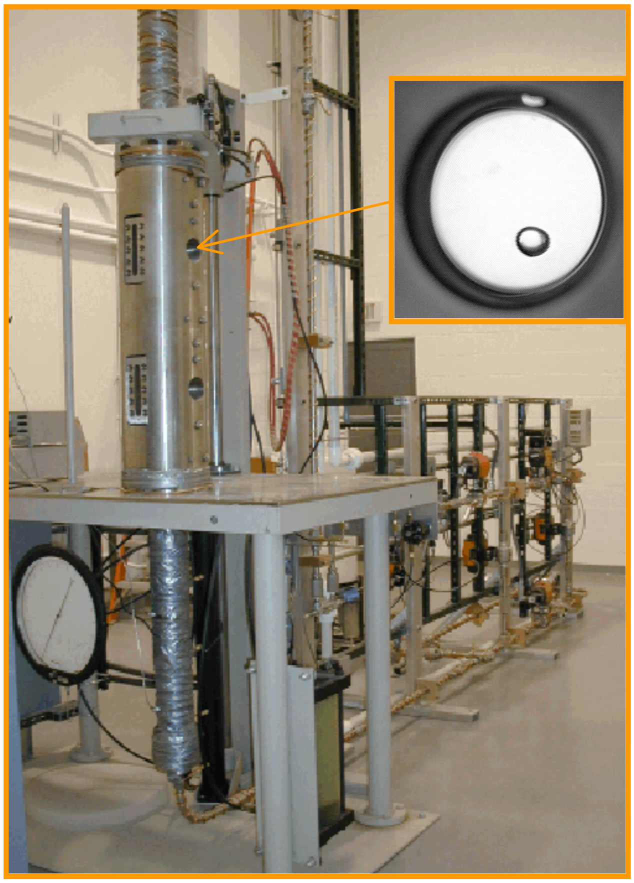


Figure 1. High Pressure Water Tunnel Facility.
Inset: CO_2 drop stabilized in the facility.

Direct Measurement of a Rising Stream of CO_2 Droplets in the Ocean
Gregor Rehder
MBARI

Gregor Rehder described research at MBARI using an ROV to directly measure the fate of a rising stream of liquid CO_2 droplets in the ocean. Experiments were carried out at 800m depth, well within the hydrate stability zone. In local waters the temperature –pressure profile gives a CO_2 hydrate phase boundary at about 325m depth. An imaging box, open at top and bottom, was constructed to keep the freely ascending droplets within visible limits. The box also provided a direct size scale, and screened out visual clutter from the ubiquitous marine snow. The droplets were imaged with a HDTV camera, providing 0.1 mm precision. For 1 cm diameter droplets the observed rise rate was 12.4 cm/sec, and the shrinking (dissolution) rate was 3 µmol/cm^2/sec. While visual contact with one droplet was maintained for about 1 hour over 400m of vertical transit, 90% of the mass loss occurred within 30 minutes and 200m above the release point.

Large Scale Deliberate Tracer Experiments

Ray Schmitt

WHOI

Large scale release of CO_2 into the ocean has much in common with a deliberate tracer release. Ray Schmitt described progress in these experiments. The preferred tracer is SF_6, which may be detected at very low concentration. This tracer also forms a hydrate, and care is taken to avoid plugging of the very small (50 micron) nozzles used to control flow. The first large scale experiment, carried out in the North Atlantic at the base of the thermocline yielded very low values (0.15x10^{-4} m^2/sec) for the vertical diffusivity, and scale dependent horizontal mixing of 0.07 m^2/sec for 100m-1km scale, 2 m^2/sec for 1-30 km scale, and 700-1500 m^2/sec for the mesocsale eddies at 300-1000km scales. A second experiment at 4000m in the deep Brazil Basin yielded higher values (10-30x10^{-4} m^2/sec) for vertical mixing, caused by tidal motion over the rough topography of the mid-Atlantic Ridge. This phenomenon of increased ocean mixing over rough topography due to tidal forcing is quite general. For CO_2 release scenarios it is the mixing at ocean boundaries over 100m-10km scale that will be critically important to investigate.

Oceanic Floats and the Deep Circulation

Russ Davis

Scripps Inst., UCSD

Russ Davis reported on the rapidly developing use of floats and gliders to test, validate, and inform, models and ideas of ocean circulation. These devices are now of modest cost (~$10K each for the floats), and can be deployed in large numbers. They are useful for study of both the large-scale general circulation, and the meso-scale eddy transport, and are programmed to change their buoyancy so as to rise to the surface periodically and report data. They can carry sensors, such as pH electrodes, for mapping a CO_2 tracer field. Since the floats are long lived (up to five years) the sensors must be long lived also. Floats sample randomly, as the flow field takes them; gliders can be directed to stay nearly in one place, or to sample oceanic sections. Their forward progress is slow, about 25 km/day.

Since injected CO_2, once diluted, is a passive tracer, then it is carried by the general circulation flow filed along isopycnal surfaces. On the decadal scale diapycnal mixing will be small, and will occur principally at topographic boundaries. The advantages of floats and gliders are that they can realistically map and predict the fate of a tracer release. The difficulties occur at inter-gyre boundaries, and where very deep winter time convection of surface waters takes place. While actively propelled AUVs are better suited for near field plume studies, the float/glider technologies offer a powerful way to study dispersal from potential CO_2 disposal sites.

Carbon Sequestration Issues at the Naval Research Laboratory

Richard Coffin
Naval Research Laboratory
Washington, D.C.

The basic microbial cycles of the ocean control many geochemical signatures. Richard Coffin reported on studies of the functioning of the microbial loop in the waters off Hawaii, with particular emphasis on $^{12}C/^{13}C$ ratios. Bacterial production in these waters is now well defined through tritiated leucine uptake experiments as 0.5-0.8 μgC/L/day. pH sensitivity studies of deep populations have been carried out, with only very small changes at pH 6. Below that a significant effect is observed.

Work in the Gulf of Mexico shows background DIC levels with $\Delta^{13}C$ as low as –32 per mille. This indicates a strong methane derived component, and indicates the need for careful assessments of differing environments. For the future work is proposed on: The pH sensitivity of the respiration function and the O_2 balance, microbial modeling of the oceanic system, and isotopic tracing of the fate of released CO_2 as it enters the biological system.

International Experiment Technical Committee Report

C.S. Wong
Institute of Ocean Sciences
Sidney, B.C.
Canada

C.S. Wong described the work he is carrying out through the technical committee in support of planning the international field experiment. This includes studying the background ocean carbon chemistry at the test site, testing and calibrating a pH sensor for deployment from an ROV or submersible, constructing an automated sampler for plume sampling from an ROV/submersible, developing a SF_6 tracer release capability, and improving models for sea water chemistry at high CO_2 – low pH.

He is using Pitzer equations for improved thermodynamic calculations, but has not yet formally included hydrates. Modeling shows that at the lower pH expected near a release point changes in metal carbonate complexing will occur, and thus for a benthic release we may expect enhanced fluxes of free metals from the sediments.

Mineral Geochemistry and Carbon Sequestration

Klaus Lackner
Los Alamos National Lab.

Klaus Lackner described progress in land based scenarios for disposal as a mineral solid. He pointed out that the fossil fuel base (particularly coal) is so very large that the temptation to use it will be unavoidable. Even with zero growth we will thus produce 600 Gt C in the 21st century; with just 2.3% annual growth we can predict a 10 fold increase in emissions. Thus a safe, minimal impact, zero legacy (permanent) and economic disposal strategy will be essential.

The scheme described here uses as a thermodynamic basis the exothermic reaction (typically 60-150 kJ/mol) in conversion of CO_2 gas into carbonate minerals. For example sepentinite and peridotite ore bodies are plentiful and easily mined. The reaction:

$$Mg_3SiO_3(OH)_4 + 3CO_2(g) \rightarrow 3MgCO_3 + 2SiO_2 + 2\ H_2O(l)$$

releases 63 kJ/mol. Studies show that the reaction goes swiftly at high temperature, and lower temperature reaction pathways are being sought.

The scheme would involve open pit mining of the mineral resource, and transport and re-fill with the carbonate mineral product. This is permanent disposal, with costs somewhat higher than ocean disposal schemes.

Progress in AUV Technology for Tracking a CO_2 Plume

John Ryan and James Bellingham

MBARI

Novel technologies for tracking the fate of a CO_2 plume are highly desirable. Ship sampling and profiling is slow and can not achieve precise positioning, and ROV systems offer powerful and sophisticated platforms but provide limited mobility for scales > 500m. One solution is to use AUVs, and John Ryan presented results from sampling the pH field of the upper ocean with an AUV system. He described use of the MIT Odyssey platform equipped with a SeaBird pH sensor for a 12 hour “saw-tooth” survey of the upper 300m of the ocean. Transiting with a speed of about 1.5 m/sec, the vehicle obtained superbly resolved data of the T,S,P,pH,O_2 fields. This permitted separation of biological and abiological processes, and detection of a harmful algal bloom and a deep suspended sediment cloud.

Jim Bellingham reviewed the present progress in vehicle development. With the addition of fuel cells ranges of 60-240 km are possible, and new vehicles will achieve 1500 km range. It is important to create a survey pattern that optimizes the space/time sampling problem for these mobile systems, and specific examples were given.

Deep Ocean Biology and CO_2 Sequestration

James Barry

MBARI

Jim Barry began by noting that any system for ameliorating the impacts of atmospheric CO_2 disposal must be considered in the light of global changes, including strong forcing of the chemistry of the biologically rich surface ocean, that are taking place today. Many deep sea animals, especially those that use vision for predation, have lower metabolic rates in the deep ocean than at shallower depths, while gelatinous animals typically do not. Globally deep sea animals have had a recent evolutionary history of a stable pH environment, and although significant changes in pH occur with depth, and between the Atlantic and Indo-Pacific oceans, animals in each ocean basin have adapted to a specific pH environment.

Changes in the extracellular pH fluid can lead to changes in intracellular pH, and the physiological cost of compensating for this has to be evaluated. Strong local CO_2 concentrations can lead to hypercapnia and torpor. Smaller changes can be compensated for, but possibly at the cost of reproductive success or prey avoidance for example. Animals that use “burst” swimming, such as the larger fish face lactic acid build up in the muscle tissues much as we do, and at lower pH reduction of lactic acid may be more difficult.

The Bohr effect, whereby blood can be loaded with oxygen and levels well above the extracellular concentration, is pH dependent, and thus oxygen carrying capacity may be limited in low pH environments.

These are just some of the issues facing deep sea physiologists seeking to understand, and provide knowledge and advice, on the CO_2 disposal strategy that might minimize harmful biological effects.

WORKING GROUP REPORTS

1) PHYSICAL CHEMISTRY ASSOCIATED WITH CO_2 SEQUESTRATION

Summary: **The Physical Chemistry group drew attention to the issues of hydrate formation as a critical control both on the release rate of CO_2 to the environment, and in creating a dense form of CO_2 that will sink within the ocean. The solution chemistry of oceanic CO_2 is well understood, but the issues surrounding hydrate formation, and the chemistry associated with liquid CO_2 contact with oceanic sediments, are almost unknown.**

“What is occurring at the CO_2-seawater interface?” This question is at the heart of all CO_2 sequestration phenomena that occur from the time and point of its release until the CO_2 either disperses to the level of a simple tracer or enters the biogeochemical cycle. The chemical phenomena associated with the natural intrusion of CO_2 from the atmosphere into the surface layer of the oceans and its subsequent fate have been defined (Sigenthaler and Sarmiento, 1993; Schimel *et al*., 1996; Wong and Hirai, 1997; Millero, F.J. 1996). However, the transport and injection of large quantities of CO_2 into the deep ocean (>500 m depth) cannot be understood and developed adequately within this existing framework.

Most indicators point toward release depths of 1500 m or greater as the most efficient and benign means of CO_2 sequestration in the ocean. Above these depths, the CO_2 would likely re-enter the atmosphere in an unacceptably short time period. Biological impacts may also be more severe at shallower depths. Moreover, at depths down to about 2700 m (depending on ambient temperature), CO_2 would be positively buoyant and create a rising droplet plume. Below this depth, injection would create a sinking plume that possibly would result in large masses of CO_2 on the seafloor.

An understanding of the fundamental phenomena associated with the CO_2-seawater interface requires information on phase equilibria, reaction kinetics, and transport phenomena, as well as identification of chemical species. The greatest uncertainty affecting the physical chemistry at the CO_2-seawater interface under conditions of deep ocean injection is the possible formation of the ice-like CO_2 clathrate hydrate ($CO_2.nH_2O$, where $6<n<8$; hereafter referred to simply as hydrate). While hydrate formation is thermodynamically and physically possible, prediction of hydrate formation and stability and the impact of hydrate on sequestration efficiency are not presently reliable. When formed at the water-CO_2 interface, surface phenomena can produce a hydrate film that occludes CO_2, determines the CO_2 diffusion rate into seawater, and varies in thickness as a function of time, shear rate, temperature etc. The kinetic determination of this film is essential to the mathematical description of CO_2 sequestration. Most models of CO_2 dissolution in the ocean do not include the phase equilibria of this film and its possible effects on mass transfer and thus offer an incomplete description of CO_2 dissolution. Although the hydrate is not stable in the open ocean owing to the low level of dissolved CO_2, its transient impacts cannot be ignored. To deny hydrates a prominent role is thermodynamically equivalent to denying the CO_2 vapor-liquid transition at depths - something universally recognized.

While being studied in the laboratory for over a century, it has been only recently that CO_2 hydrate was formed and observed in the deep ocean (Brewer *et al*., 1998, 1999). Both in the ocean and in laboratory simulations, hydrate is observed to occur either as discrete particles or as a skin on drops or larger masses of CO_2. Visual detection methods are commonly used; however, hydrates can be difficult to detect visually, especially if they occur as very thin films on liquid CO_2 drops or larger masses or as discrete, nearly transparent particles.

A hydrate film can have a significant impact on the dissolution of the entrapped liquid CO_2 into the ocean, as demonstrated by both laboratory and *in-situ* experiments (Warzinski *et al*., 2000; Aya *et al*., 1997; Nishikawa *et al*., 1995; Peltzer *et al*., 2000). Such an occurrence during a mid-water (depths between about 500 m and 2700 m) release can complicate sequestration attempts in that the CO_2 would rise farther in the ocean water column before complete dissolution, ultimately resulting in shorter residence times in the ocean. On the other hand, formation of a hydrate film on sinking CO_2 drops (depths greater than about 2700 m) could enhance the efficiency of sequestration by facilitating transport of the CO_2 to greater depths before dissolution. It should be possible to design injection technologies that create sufficient CO_2/water mixing that sufficient hydrate is formed so as to create a sinking mass.

At depths greater than about 3000m the density of liquid CO_2 is sufficiently greater than the surrounding sea water that it will remain on the sea floor as a separate fluid phase, possibly pooling, or spilling to greater depth. Here the interaction with marine sediments must be considered (Harrison et al., 1995). We may expect issues of considerable complexity to arise accompanying hydrate formation, and as dense CO_2 saturated water penetrates the sediment pores (Figure 1).

While the thermodynamics of CO_2 hydrate in water and seawater are known, metastable hydrate phases can exist which confound prediction capabilities. Additional deviations from existing modes for pure CO_2-H_2O can also arise from impurities in the CO_2 stream, such as H_2S, SO_2, N_2 or O_2, which may form mixed hydrate with the CO_2. Such a mixed hydrate could have markedly different formation characteristics and stability in the ocean compared to pure CO_2 hydrate.

The formation of hydrate in transportation pipelines and delivery systems can also be a problem if any water is present and the pressure and temperature are above 50 bar and below 10^oC, respectively. Similar problems in the natural gas industry have resulted in considerable investment to understand and control this problem.

Another important but overlooked factor in hydrate stability is the heat of hydrate formation. Hydrate formation and stability in deep oceans could depend on the dissipation rate of the heat released. Aya *et al*. (1997) have measured the heat of hydration of CO_2/water mixtures. Present modeling simulations do not account for the heat of reaction that evolves during hydrate formation.

Apart from the possible transient effects of hydrate formation, other issues remain unresolved concerning the physical chemistry of direct CO_2 injection. The reaction of CO_2 --especially if any impurities, such as H_2O, H_2S, or SO_2, are present-- with the materials used to pump, transport, and deliver the stream needs to be understood. Understanding the impact of CO_2 and its trace impurities on ocean and sediment chemistry is also important.

Figure 1. Image of a mass of CO_2 hydrate formed on the sea floor at 3,600m depth by penetration of liquid CO_2 into the sediment followed by hydrate nucleation (Brewer et al., 2001).

Significant accomplishments are possible over the next eight years mostly through laboratory and small-scale field testing. Critical information can be obtained that will answer many of the unknown physical chemistry issues and therefore, help to develop the science base to enable an accurate societal evaluation of the efficiency of CO_2 sequestration in the ocean. It is also important to pursue key large-scale experiments. While more costly, time consuming, and difficult to implement, they are the only means to obtain certain types of data and to validate the conclusions of smaller-scale work and modeling efforts. The study of natural CO_2 vents, such as those found by Sakai *et al*. (1990), can perhaps provide a fruitful, less contentious alternative in some cases. In particular, such sites may provide useful information on biological impacts of long-term exposure of ecosystems to elevated levels of CO_2.

During the next eight years, the following research initiatives pertinent to physical chemistry issues associated with direct oceanic sequestration of CO_2 need to be emphasized. The first five initiatives encompass overarching activities; whereas, the other nine initiatives are more targeted toward specific research goals. The accompanying chart displays a proposed eight-year timeline for structuring a program incorporating these initiatives. An estimate of the relative difficulty of each initiative is also indicated.

PROPOSED RESEARCH INITIATIVES

Overarching Research Initiatives

1. Inventory facilities available for laboratory and small field-scale work.

While much has been learned relative to oceanic sequestration in the laboratory and field, considerable work still needs to be performed. Rather than develop new laboratory/field facilities, which are extremely costly, it is important to utilize already constructed and proven experimental facilities to make efficient, quantitative and phenomenological measurements. Molecular modeling should only be used in the cases where it is impossible or too costly to obtain experimental measurements. In particular, time dependent measurements are needed, with emphasis on direct measurements of the hydrate phase rather than associated phases.

Possible sites for small-scale field tests should provide access to depths of 1500 to 4000 meters for meaningful evaluation at conditions that ensure long-term sequestration of CO_2.

The goal of this Initiative is to provide a listing of national and international facilities that have been or can be used for sequestration or hydrate research and describe the specific capabilities that are pertinent to the oceanic sequestration field. An inventory of laboratory facilities for performing CO_2 sequestration research was performed several years ago by RITE for facilities in Japan. This information should be updated and included in the proposed inventory.

2. Develop a comprehensive accounting of the chemical pathways of released CO_2.

Much is understood concerning the chemical pathways associated with CO_2 entering the oceans by natural means, especially through the air-sea interface. The impacts of more concentrated releases of CO_2 on these pathways and the occurrence of any new pathways needs to be defined. Resolution of this issue is vitally important for public acceptance of any form of oceanic CO_2 sequestration. Also, the estimated outcome of any CO_2 sequestration scenario has to be evaluated in comparison to the sequestration now taking place in the surface layer of the ocean. The goal of this Initiative is to provide a detailed description of the possible fate of CO_2 introduced into the deep ocean and highlight areas were insufficient information is available that is critical to this issue.

3. Address questions of sample representativeness, experimental accuracy, and reproducibility.

The presence of hydrates in oceanic sequestration not only complicates the sequestration process it also presents problems in obtaining meaningful laboratory data. Nearly all of the information on hydrates of different gases has been obtained from laboratory studies. While providing fundamental thermodynamic data and many useful insights, the nature of hydrate formation and dissociation present problems that must be overcome if laboratory data are to be useful in understanding the behavior of hydrates in natural environments. Hydrate formation and growth are affected by many variables, which can even include the design and configuration of the laboratory reactors themselves. This complication can even be extended to small-scale field experiments that often use confining devices in the execution of the experiment. Thus the interpretation, comparison, and extension of data to the open ocean can often be difficult.

Reproducible samples of hydrates can be made in the laboratory when all of a melting ice phase in contact with a hydrate-forming gas is converted to hydrate (Stern *et al*., 1998). However, in the field, especially for oceanic sequestration, hydrate does not form from melting ice but is either formed at the water-CO_2 interface or from CO_2 dissolved in the water. While some issues may be best answered using pure CO_2 hydrate, others require the use of laboratory systems that can prepare hydrate or hydrate-encased CO_2 samples in a manner analogous to what would occur in the ocean.

The goal of this initiative is to define the issues and problems associated with obtaining robust, reliable information from small-scale laboratory and field experiments on the various aspects of ocean sequestration, especially concerning the roles and impacts of hydrate. Guidelines will be prepared to assist experimentalists in avoiding known pitfalls and in designing and performing experiments to obtain meaningful data.

4. Conduct small-scale laboratory and *in situ* experiments to provide needed data.

In general the amount of fundamental knowledge gained is inversely proportional to the size of the experiment. For example, the primary objective of the planned 2001 field experiment in Hawaii, where approximately 50 tons of CO_2 will be discharged at 800 m in the ocean, is to obtain data that will be applied to develop and validate near-field CO_2 plume models. It is much easier to perform small-scale experiments, such as those done by MBARI's injection of 7L of CO_2 into the ocean. The rise or fall of a few small droplets of CO_2 may be a good pilot for determining the outcome of larger experiments, placating environmentalists with the thought that "only a gas tank of CO_2 is being injected into the ocean". Many such small-scale laboratory and *in-situ* experiments can be done for the time and cost of such a large-scale experiment, to be sure for example, that models from small scale experiments include the correct phase equilibria before attempting to perform transport calculations.

All of the focused research initiatives (6 –14) will require considerable laboratory and small-scale field experiments to achieve their goals. Initial work on this Initiative will be to prepare a roadmap using the information from Initiative 1 to outline both the magnitude of work for each Focused Research Initiative and the possible facilities and research teams that could perform such work. Possible collaborations will be noted. This work will also highlight the need for new or significantly modified facilities and equipment.

5. Carry out large-scale *in situ* and natural lab experiments as end-point model confirmation.

Appropriate large-scale experiments are ultimately required to validate information obtained in smaller-scale work and to discover any unknown unknowns that would only occur in realistic situations. Moreover, large-scale experiments can offer unique opportunities to address broad, multi-disciplinary issues rather than tightly focused research themes and provide a venue for extensive information sharing and collaboration between participating researchers. The goal of this Initiative is to provide assessment of the need for such experiments and to integrate the expanded knowledge base resulting from the Expert's Workshop into the existing efforts of the international research community already associated with such efforts.

This Initiative will also explore the use of seafloor vents from which CO_2 is discharging as natural laboratories for obtaining information relative to proposed sequestration scenarios. These may be ideal sites to study the formation of hydrates on a large scale and to explore possible changes in hydrates over time by investigating hydrate deposits of different ages at the site. Such information can help in the development of protocols for staging large-scale CO_2 discharges in experiments on the seafloor. The location of such known vents and estimates of the costs to utilize them in the manner described will be part of the initial work on this Initiative.

Focused Research Initiatives

6. Develop sub-models and parameters for CO_2-hydrate-seawater interface dynamics, which are vital to hydrodynamic modeling efforts

Hydrodynamic models are used to predict the transport of carbon-enriched seawater away from the CO_2 injection or deposition site. This information is used both to determine carbon concentration fields that are of importance in biological assessments, and to predict the efficiency of sequestration through outgassing to the atmosphere as a function of time. At present such models do not explicitly include hydrate effects, due to the lack of validated parameters or sub-models for this species (Alendal and Drange, 2001), but rather attempt to approximate hydrate effects on transport by varying mass transport and drag coefficients. At present there are even minimal direct thermodynamic (time-independent) measurements of the hydrate phase; the time-dependent dynamic behavior has only begun to be approximated. In order to do the simulations accurately, it is crucial to have the CO_2 source terms correct. The major uncertainties at present are related to the dissolution rate (mass transfer), especially when hydrate is formed at the CO_2-seawater interface. This quantitative description, as a function of temperature, shear, etc., is vital to understanding the fate of CO_2 dispersing in the ocean from either a mid-water injection or a deep release. A sub-model is also required that accounts for the heat of hydrate formation. The effect of the CO_2 hydrate formation heat release and subsequent dissipation on local temperature and hydrate stability must be simulated.

The activity on this Initiative should be ongoing throughout the 8 years period but with main effort during the first 3-4 years. An important aspect of this task is communication. As new chemical and physical information is developed it must be relayed to those involved in developing the models. The modelers have to be diligent in identifying their uncertainties and needs. Experimentalists must keep the modelers needs in mind when designing, performing and analyzing experiments.

The work on this Initiative is very challenging. Certain characteristics of CO_2 hydrate make it difficult to establish an accurate sub-model/parameters for CO_2-hydrate-seawater interface dynamics. For example, the hydrate membrane covering a CO_2 droplet is very thin (on the order of a micrometer), but it is a solid film that will dramatically reduce the dissolution rate of CO_2 into the ocean. The hydrate membrane also easily elongates with stress by a mechanism that is not understood. The changing shape and thickness of the membrane add additional complexity to this problem. The concentration of dissolved CO_2 is also important in defining the stability of the hydrate and dissolution rate of any liquid CO_2 entrapped by it. To better understand these phenomena, laboratory measurements should be encouraged by researchers capable of simulating the oceanic environment and sequestration release scenarios.

7. Develop satisfactory analytical tools for detecting and characterizing hydrates

The recognition of the fundamental importance of what occurs at the CO_2-seawater interface calls for the development of improved analytical tools and protocols to document all steps in the formation of hydrates. It is difficult to image hydrates in their earliest stages of formation; instrumentation is needed to detect even small volumes of hydrate. Such tools also need to be able to characterize the specific chemistry of the hydrate (including impurities) as well as structural type and degree of crystallinity. Such information is essential to understanding the stability and longevity of hydrates on the seafloor.

Currently there are three principal tools for measuring hydrates directly: (1) diffraction, (2) NMR spectroscopy, and (3) Raman spectroscopy. Over the last 75 years most measurements have been made of the hydrate-adjacent phases (e.g., P, T, or salinity changes) and not the hydrate themselves. This has led to a number of errors in the literature. For example, until a few years ago, it was widely believed that CO_2 occupied only the large cages of the SI hydrate cavity; with polarized Raman measurements, we now know that both hydrate cavities are occupied. As a second example, using all three above techniques it has been confirmed that over 50% of the hydrate data for $CH_4+C_2H_6$ were assumed to be the incorrect crystal structure, with associated quantitative errors in pressure and temperature description.

Other properties of the hydrate also are important to measure such as refractive index, density, elasticity, mechanical strength, and electrical and thermal properties. For example, investigating hydrate refractive index is important because many experiments have and will rely on visual observations to identify hydrate occurrence. The similarity of the refractive indices of seawater and CO_2 hydrate, especially at conditions approaching those at the ocean floor, have been inferred from experimental observations (Warzinski *et al*., 2000; Brewer *et al*., 1999); however, no measurements of CO_2 hydrate refractive index exist. Only one value (1.34) for a THF hydrate has been published by Davidson *et al*. (1986). Methods are needed to obtain more data.

The goal of this Initiative is to develop a new generation of analytical tools and procedures for accurately determining important hydrate properties.

8. Develop satisfactory analytical tools for quantifying CO_2 and seawater chemistry *in situ*.

Small-scale experiments to both release CO_2 into deep ocean and to create CO_2 pools and associated hydrate masses on the seafloor already have shown that there are important factors in the natural environment that cannot be simulated fully in the laboratory (Brewer *et al.*, 1999). In order to understand how injected CO_2 will react in the ocean water column or on the seafloor, additional experiments need to be carried out in the natural setting and appropriate analytical tools need to be adapted to this harsh environment to monitor the fluid chemistry *in situ.* The goal of this Initiative is to develop the needed analytical tools capable of working in the harsh environments associated with deep ocean sequestration. NMR and Raman techniques appear to be the most promising candidates.

9. Develop models for hydrate formation and dissolution in seawater.

The goal of this Initiative is to develop improved hydrodynamic models that are integrated with biological impact and sequestration effectiveness research. Such models need to incorporate the agglomerating nature of CO_2 drops that have been observed in the laboratory and in *in-situ* experiments. Such agglomeration results in higher ascending velocity, which accelerates the agglomeration tendency itself, which ultimately results in an increase of un-dissolved CO_2. Hydrodynamic models also need to be integrated with physical chemistry parameters. This is important in accounting for the affects of dissolved CO_2 on the formation and stability of hydrate particles or skins and on the dissolution rate of masses of CO_2 on the seafloor.

10. Understand the impact of impurities of real discharge gas mixtures on the dissolution of CO_2 in seawater and the chemical effects of the discharge.
It is unlikely that a pure stream of CO_2 will be transported and discharged in any sequestration scenario. This Initiative will focus on research to determine the expected levels of impurities from the most likely existing and future industrial separation and capture schemes. Small amounts of impurities can have a major impact on CO_2 sequestration. For example, minute amounts of hydrogen sulfide and particulate matter can drastically effect the thermodynamic and kinetic stabilities, respectively, of CO_2 hydrates in the ocean. Due to their toxicity, H_2S hydrates have seldom been measured, and heterogeneous nucleation experiments have not been done in a repeatable fashion.

11. Investigate potential means for changing hydrate kinetics using promoters or inhibitors.
Formation of CO_2 hydrate in transportation systems used for ocean sequestration may occur if any water is present in the system. It may be more cost effective to add small amounts of kinetic inhibitors if complete dewatering of the stream is cost prohibitive. In this Initiative, research will be performed to develop low-cost, low-dose inhibitors to insure reliable operation of CO_2 transportation and delivery systems. A comparative cost analysis will also be performed.

It may be possible to utilize hydrate formation to improve the deep ocean sequestration concept. Forming CO_2 hydrate under controlled conditions can result in a hydrate that sinks through the ocean water column while dissolving more slowly than liquid CO_2 without hydrate. This would minimize both the injection depths required and the impacts caused by unacceptable pH changes near the point of injection.

Prior work has shown that it is possible to both inhibit and to promote rapid hydrate formation using kinetic inhibitors (Sloan *et al*., 1998). Most of the research has been performed for natural gas hydrates, whereas virtually nothing has been done in this area for CO_2 hydrate. However, the mechanism is well established and the knowledge should be transferable. Research on this Initiative will seek to extend this knowledge to the CO_2-seawater system with the objective of achieving better long-term stability of CO_2 in the ocean.

12. Develop an understanding of the insulating effects of a CO_2 layer or hydrate layer on sediments.
In the deep release scenario, a large mass of liquid CO_2 with hydrate may rest on the seafloor for extended periods of time. This layer may limit the normal exchange of chemical species between the seafloor community and the ocean, as well as introduce a higher level of CO_2 into the sediments. Research on this Initiative will seek to understand the transport phenomena and diffusivities of O_2, H_2S, $SO_4^{=}$, and NO_3^- in the CO_2 hydrate mass and the penetration of CO_2 into the sediments. This would provide parameters for the evaluation of the biological effects of CO_2 sequestration on benthic communities. The dissolution rates of CO_2 hydrate masses will be measured.

13. Investigate the leaching effects of CO_2 on the seafloor sediments.

There is well-founded concern that the introduction of CO_2 onto the seafloor will alter certain indigenous minerals, and will induce formation of other minerals, in addition to formation of the CO_2 clathrate hydrate. These predicted changes are based on the calculated changes in seawater composition, particularly pH, that arise upon the dissolution of the introduced CO_2 (Harrison *et al*., 1995; Bohrmann *et al*., 1998; Archer *et al*., 1998; Clennell *et al*., 1999). This Initiative will include experiments in which real seafloor sediments of the types found in proposed/considered sequestration sites are exposed to CO_2 in seawater solutions under conditions mimicking those on the seafloor.

14. Investigate other possible solid phases in which CO_2 could be sequestered on the seafloor.

Portions of the seafloor are rich in calcium carbonate (the minerals calcite and aragonite); other parts have abundant carbonated apatite (phosphatic sediments whose chemistry resembles that of animal bone and teeth). The work on this Initiative will pursue a better understanding of the formation and stability of carbonated phases that are known to exist on the seafloor with the goal of providing additional insights into and options for permanent CO_2 sequestration in the deep ocean.

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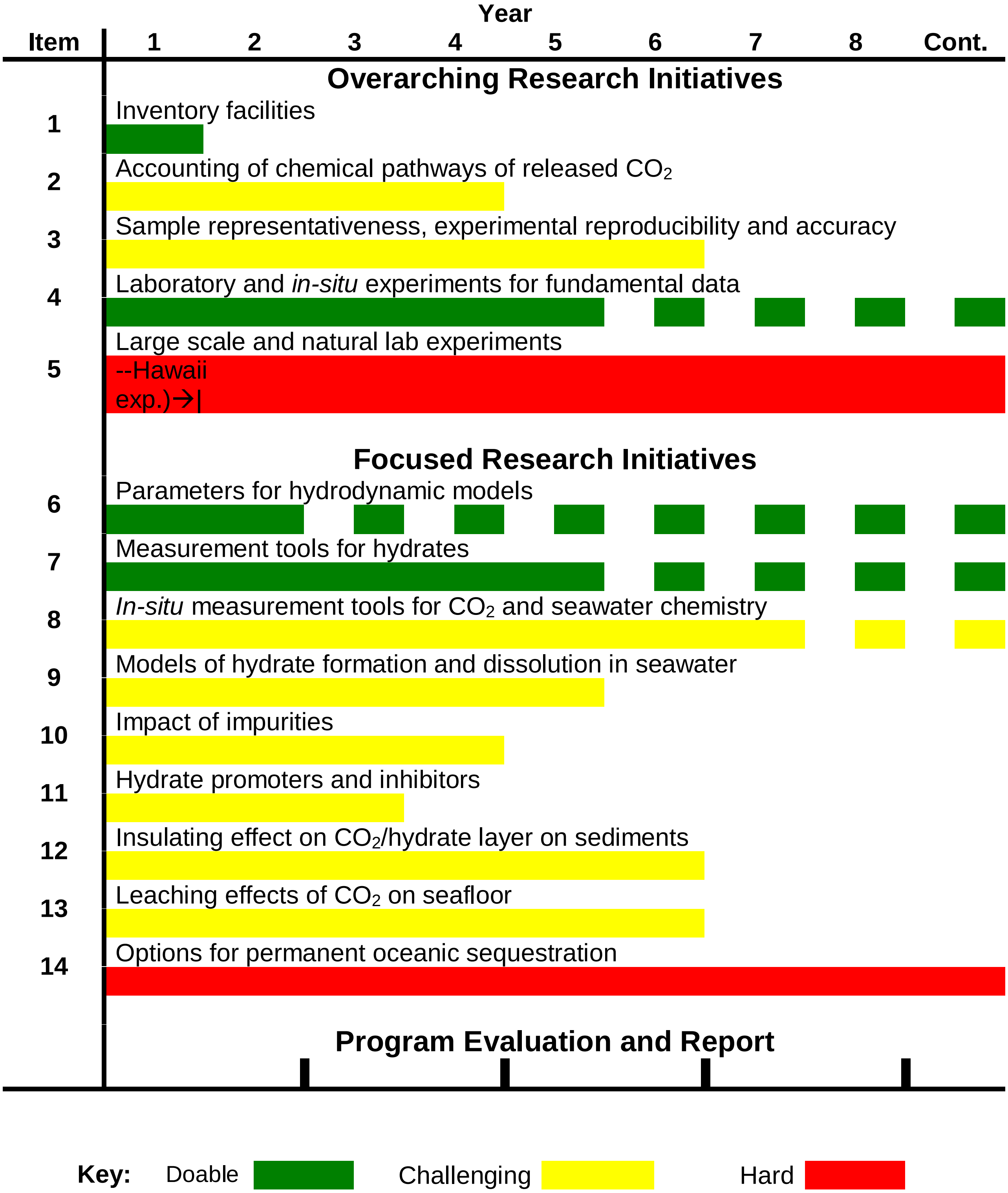

2) Studies of Ocean Physics Associated With Carbon Sequestration

Summary: **The ocean physics required for CO_2 sequestration studies require new knowledge of ocean mixing at critical scales ranging from plume dynamics where the large density gradients created must play a role, to the 100m-10km scale where processes are not well observed. Studies of the enhanced mixing due to tidal interactions with local topography will play a critical role in defining processes at specific sites. Interaction with models of global ocean circulation, and associated climate studies will be essential.**

Additional research is needed to understand ocean physics well enough to assess:

- Any potentially significant biological responses to the injected CO_2; and
- The efficiency with which directly injected CO_2 remains sequestered from the atmosphere.

Three kinds of study, requiring in turn increasing precision and completeness, will be needed:

a. A range of preliminary studies will be needed to select between different methods of injection (near bottom injections, CO_2 lakes, or moving-ship deployments) and between potential injection sites;

b. Detailed site surveys will be needed at any potential injection site in order to prepare accurate predictions of efficiency and bio-impact; and

c. Any actual injections will need to be monitored for both biological impact and efficiency.

A complete description of the physical factors affecting efficiency and biological impacts would involve almost every are of ocean physics research. At the MBARI meeting an effort was made to identify the information most important in the initial general evaluation of direct injection that is not now available.

Biological Impacts

Biological impacts of a CO_2 injection become more severe as organisms are exposed to higher concentrations and longer durations. A complete physical description for assessing biological impacts therefore includes the probability of exposure to a given concentration or pH for a given duration for organisms resting on the bottom, drifting with the water, or swimming. A more feasible description is the map of mean concentration resulting from injection and the map of extreme CO_2 concentrations and pH that are likely to be encountered.

Phenomenologically, the mean concentration will be determined by initial conditions for plume spread set by the injection method and by the range of displacements parts of the plume will undergo as a function of time since injection. In this sense an irregularly oscillating broad-scale flow can disperse the plume although it does not significantly stir or mix it. Extreme concentrations, on the other hand, depend on stirring motions that will accelerate the rate at which the injected material is mixed with the ambient waters. Lateral dispersion that largely determines the mean concentration can be measured with current-following floats. But as tracers spread, they are stretched into streaks of high concentration with regions of very low concentration between. The processes that determine how well mixed a plume will be can only be measured using a tracer that serves as a proxy for the injection plume. The same tracer can also determine the diapycnal spread of the plume. Presently available tracer results suggest that injected material will not be well mixed until ambient ocean motions have stirred it for months. Over that time a weak current of the O(1 cm/s) would advect the plume over distances of O(100 km) and disperse it by ocean eddy motion over distances over tens of kilometers.

In the immediate vicinity of the discharge point and the associated plume of liquid CO_2/water /hydrate mixtures. Outside this will be a region of high dissolved CO_2 and substantially reduced pH. How large will the region of substantial potential biological impact be? In order to gain perspective, consider a discharge rate, Q, of 10 m^3/sec (i.e. approximately 10 t/sec, or 300 Mt/yr) of liquid CO_2. A 10% increase of dissolved inorganic carbon (DIC) above natural background levels (i.e. $\Delta DIC \approx 250\ \mu mol/kg$) is a rough guide to the concentration at which significant impacts may begin to disappear. This corresponds approximately to a pH change of 0.5, and is a level broadly comparable to the natural difference of DIC and pH between surface and deep waters due to biological processes and the level of pH change at which moderate/severe biological effects on animals are to be expected. Since pure liquid CO_2 corresponds to about 25 mol/kg, achieving this concentration level requires dilution by a factor of 10^5. To reach this level therefore requires the dissolution of the discharge into a volume transport or diffusive exchange corresponding to about 10^6 m^3/sec, i.e. 1 Sverdrup. Steady-state injection into a broad-scale ambient current would produce a plume whose width, and to a lesser extent height, would grow downstream from injection. If the current were O(1 cm/s), as is typical of the deep ocean below 1500 m, significant impacts would be found until the downstream plume had spread, for example, to a vertical extent of 200 m and a width of order 500 km. This might not happen until several thousand kilometers downstream of the injection site.

A further order-of-magnitude calculation estimates the areal extent of the pool or stream of liquid CO_2 that might form and persist on the bottom in the immediate vicinity of the discharge point, if this is situated at a depth exceeding 3000m. First estimates of the dissolution rate at a liquid CO_2 surface at 800m depth are 3 $\mu mol/cm^2 sec$ (Brewer et al 2001), but there is some evidence that the rate is lower by a factor of 3 or so at greater depths (Brewer, pers. comm.). Taking a lower value of 1 $\mu mol/cm^2 sec$ as a nominal figure, the dissolution of 10^5 mol/sec of CO_2 would therefore require a surface area of 10^{11} cm^2, i.e. 10^7 m^2, representing a surface extent of about 3 km by 3 km for a pool, or perhaps 30km by 300m for a stream.

These order of magnitude estimates at least show that it is vital that the mean and extreme concentrations from an injection be predicted before any action undertaken. This will require that the dispersal and stirring characteristics of the ocean at any potential injection site be determined and used to model realistic plume behavior. This will require that models be developed that extend models of the injection, models that span O(1 km), to the oceanic scale of O(100 km) upon which today's ocean circulation models work well. We are not aware of models of this type, but there are oceanographic models on this scale that could be straightforwardly matched to the engineering models that describe behavior in the immediate neighborhood of the injection. The ocean models will, however, require site-specific observations of dispersal and mixing in order to tune their representations of ocean turbulence.

Fortunately, recent technical advances in detecting extremely small quantities of the tracer SF6, in deploying and sampling tracers, and in current-following neutrally buoyant floats make it feasible to gather the information needed to tune injection and ocean models. To do this a combination of an easily measured fluorescent dye for the near field (of O(10 km) from the injection site) and SF_6 for the far field spanning distances of O(1000 km).

Fluorescent dyes are easily measured from ships, moorings, and autonomous underwater vehicles. This makes it feasible to densely sample the early spread of a locally injected dye for a few days as it disperses and is strained over tens of kilometers. After this point, dye concentrations decrease to the limit of detectability. For the longer time scales and larger space scales needed to fully assess biological exposure it is necessary to use a tracer like SF_6 that can be detected at dilutions as great as 10^{10}. Sampling SF6 is now done only from ships but it should be possible to develop techniques to allow sampling for later analysis from platforms with lower operating costs. Even without these advances, it is possible to map out the extent and degree of mixing of SF_6 plumes as they disperse over times of O(10 years) and O(1000 km).

To more fully interpret the evolution of dye and tracer fields (and to speed sampling of SF_6 plumes) it is very helpful to also deploy neutrally buoyant floats as a third "tracer" that disperses along with the dye and SF_6. Because they are much more easily tracked than tracers, floats are particularly useful in extending the area sampled and filling in between filaments of the tracer plume.

Unlike the studies discussed below that are needed to improve the accuracy of efficiency projections, the measurements needed to predict the biological impacts of injections are primarily of interest to the direct injection problem and therefore would likely need to be carried out mainly for that purpose. The magnitude of one such study is significant but not unreasonable. A total of about 10 months of ship observation, a couple of AUV months and about 50 neutrally buoyant floats would constitute an appropriate level of activity. Two initial studies focused on injections near 3000 m depth are recommended, one over a much deeper abyssal plain and another along a continental slope. The eastern Pacific is, at this point, the location near the U.S. that is most attractive as a site for direct injection.

Efficiency

The most important consideration in selecting a site for efficient direct-injection sequestration is that of injection depth, or more importantly the density of the water into which injection will be made. The simplest physical estimates of the turnover times of the ventilated portion of the ocean suggest that CO_2 injected into intermediate waters, or at less dense levels, will be brought into contact with the atmosphere within a few decades. This is confirmed by predictions from a wide range of ocean circulation models. This rapid ventilation would return CO_2 to the atmosphere and decrease injection efficiency. For this reason, we have focused attention on the physics needed to predict the efficiency of injections into deep waters, below intermediate waters.

The efficiency of the ocean in retaining sequestered CO_2 can only be estimated by making simulations in ocean models. Ocean general circulation models (OGCM) have been used to estimate efficiencies. These models describe ocean circulation and mixing at the global scale. Recent comparison of such simulations in seven OGCMs provides a first estimate of associated uncertainties. OGCMs used for sequestration studies have all employed coarse-resolution grids, which are unable to resolve important sub-grid-scale processes (e.g., eddies, boundary currents, convection, etc.). Properly accounting for these processes could substantially alter model predictions of CO_2 sequestration efficiency. Global-scale OGCM's are now available that do resolve these processes. However their high resolution means that they are expensive to run and can only be integrated for relatively short periods, about 10 years.

An important challenge is then to develop methods to make much longer simulations in these high resolution OGCMs. Simulations of millennia are required to evaluate the present-day ocean carbon cycle and its perturbation due to deep CO_2 injection. Ocean carbon-cycle modelers already accelerate coarse-resolution simulations by exploiting archived fields of advection and mixing from an OGCM (offline), thereby avoiding the costly re-computation of ocean dynamics (online). In the future, further acceleration of offline simulations could be obtained by switching from an Eulerian to a Lagrangian approach. An Eulerian approach tracks fluxes into and out of fixed grid points; a Lagrangian approach tracks concentrations of moving water parcels and their exchange with one another. Such an approach has been used successfully in atmospheric chemistry modeling (Taylor, 1989). Work with atmospheric models suggests that a Lagrangian approach could accelerate simulations by 100 times or more, but that is highly model dependent.

Model evaluation would be a critical component during development of a Lagrangian, high-resolution offline ocean model. For such an effort, one would need to clearly demonstrate the skill of the daughter Lagrangian ocean model to reproduce tracer distribution patterns of the parent online Eulerian model, and one would need to compare both models with the real ocean. A crucial test would be comparison of recently injected SF6, an inert tracer. Injections of SF_6 would be most useful in boundary currents where injections are likely to occur. The model would also need to reproduce the distribution of ocean ^{14}C to assure that its global efficiency is not severely biased.

When the spread of injected CO_2 in the ocean, particularly distributions resulting from deep injections, are compared between different models or with our present descriptions it becomes clear that the Southern Ocean, particularly ventilation of North Atlantic Deep Water south of the Antarctic convergence, needs to be better known before projections of efficiency on the multi-century time scale can be accurate. The water densities at which a deep injection of CO_2 would be made reach the surface only in the near-polar oceans where the surface water is cold and examination of the global ocean circulation suggests that much of the CO_2 injected at depth will eventually return to the atmosphere via the surface waters in the Southern Ocean. Depending on the depth and the ocean basin of injection, the duration of sequestration might be between a few centuries or 1000 years or more. While only the North Atlantic is ventilated in the northern hemisphere, the deep waters of the Atlantic, Indian and Pacific all reach the surface in the Southern Ocean. The Atlantic has a turn-over time of about 250 years, whereas the Indian and Pacific deep water reaches the surface much more slowly. Information on the spatial variations in abyssal mixing needs to be incorporated into models so that the pathways and rates of deep-water flow are accurately represented (Ledwell et al, 2000). While the general principles of Southern Ocean ventilation are clear, the details are not well known. This is reflected in the fact that many of the differences in sequestration efficiencies found by the models reflect differences in their treatments of the Southern Ocean. These discrepancies reflect fundamental weaknesses in our knowledge about Southern Ocean processes. One of the most important ways in which we could increase confidence in our prediction of sequestration efficiencies would be by improving our understanding of these processes.

For example, we are unsure by what pathways water from the deep sea returns to the surface in the Southern Ocean. The waters at mid-depth are thought to derive from a blending of Atlantic, Pacific and Indian ocean deep waters, there being isopycnal exchange between these water masses and the circumpolar deep waters. Isopycnal mixing rates have been observed to vary greatly in the tracer release experiments, yet little is known about what controls such changes. Circumpolar waters feed upwelling water in the Antarctic polar zone, and upwelling water is removed from the surface either by being driven northward into the subantarctic zone, or by being converted into very dense water that sinks to the bottom near the Antarctic shelf. During its sojourn at the surface the water could lose some of its injected CO_2 burden to the atmosphere depending upon the ocean-atmosphere pCO_2 gradient established in time and place.

Critical details important for calculating rates of loss are poorly known. We do not know how long upwelling water remains at the surface and with what depth of mixed layer. Some of the northward-going surface water may cross the various circumpolar fronts and contribute to the formation of intermediate waters which feed back into the major ocean basins at shallower levels, but how much? What controls the rate of bottom water formation? To answer these questions we need a better understanding of cross-front transport and mixing, the amounts and rates of deep convection and rates of diapycnal water mass transformation.

Convection is a critical process that is inadequately modeled in present OGCMs. Real convection in the oceans takes place in relatively small, intense, plumes, which cannot be resolved in present circulation models. Different approaches to the treatment of convection result in very different penetration of convective layers, and these differences lead to divergent predictions about the rates of ventilation of Southern Ocean waters. Convection can be studied by release of tracers and neutrally buoyant floats, and a more complete picture is slowly emerging as a result of studies in the Labrador Sea and Greenland Sea. There have been very few studies in the Southern Ocean however. Studies that have varied the way in which convection is handled in circulation models have led to radically different predictions about the rates of uptake of anthropogenic tracers, and most probably would give different answers for the out gassing of injected CO_2 as well.

Diapycnal mixing is also poorly represented in models; most treat it as a uniformly small vertical diffusivity. However, recent progress in tracer release experiments and microstructure measurements has shown that changes in internal wave levels contribute to large variations in diapycnal mixing. That is, at mid-latitudes, it has been shown that the turbulent dissipation rate can be related to the finescale vertical shear of horizontal currents (Gregg, 1989). Also, the tracer release experiments at 300 m depth in the North Atlantic thermocline, and 4000 m depth in the Brazil Basin, have shown that the traditional microstructure measurements and models do a good job of estimating the diapycnal mixing (Ledwell et al, 1998; Ledwell et al, 2000). The Brazil Basin data suggests that tidal flows over topography are the source of intensified internal waves and strong turbulent mixing above the rough topography of the mid-Atlantic Ridge.

These findings reinforce a suggestion by Polzin and Firing (1997) that elevated fine-scale shears in the Antarctic Circumpolar Current (AACC) could be providing a particularly large diapycnal diffusivity (4.4×10^{-4} m^2/s) below 1000 m depth, particularly near topography. The elevated observed shears are likely due to internal lee-waves generated by the mean bottom flows over rough topography. Many segments of the AACC have significant bottom topography that could contribute to enhanced internal wave generation and mixing. However, no microstructure measurements at all have been made in the Southern Ocean. Similarly, no tracer experiments have been done there. Tracer release experiments are especially valuable for estimating the rates of horizontal dispersion and mixing. In addition to enhanced shears, many Southern Ocean areas have elevated levels of interleaving in temperature and salinity profiles that are suggestive of strong cross-frontal mixing processes. Knowing the mechanisms and spatial patterns of mixing in the Southern Ocean is crucial for understanding the upwelling and conversion of deep waters (NADW) into Antarctic Bottom Water or Antarctic Intermediate Water, and how effectively CO_2 can be communicated to the atmosphere.

Ultimately, confidence in model predictions of direct-injection sequestration will depend on how well the models used are able to simulate and explain other features of the general circulation. In this respect the goals of applied sequestration research are parallel with academic interests in other phenomena that depend on the ocean's ability to exchange material with the atmosphere and to transport it. Research in the natural carbon cycle and in the distribution of various geophysical and time-tagged tracers addresses many of the same problems. Thus the community that has long studied deep-ocean hydrography and tracer distributions can be expected to provide information that will improve calculations of sequestration efficiency. Collaboration with these communities, perhaps through inter-agency support of the U.S. carbon program, might be a cost-effective way to improve and validate the OGCMs used to predict efficiency. Commissioning a few hydrographic/tracer scientists to examine model runs and analyze them much as they might the ocean itself might open an avenue to this community.

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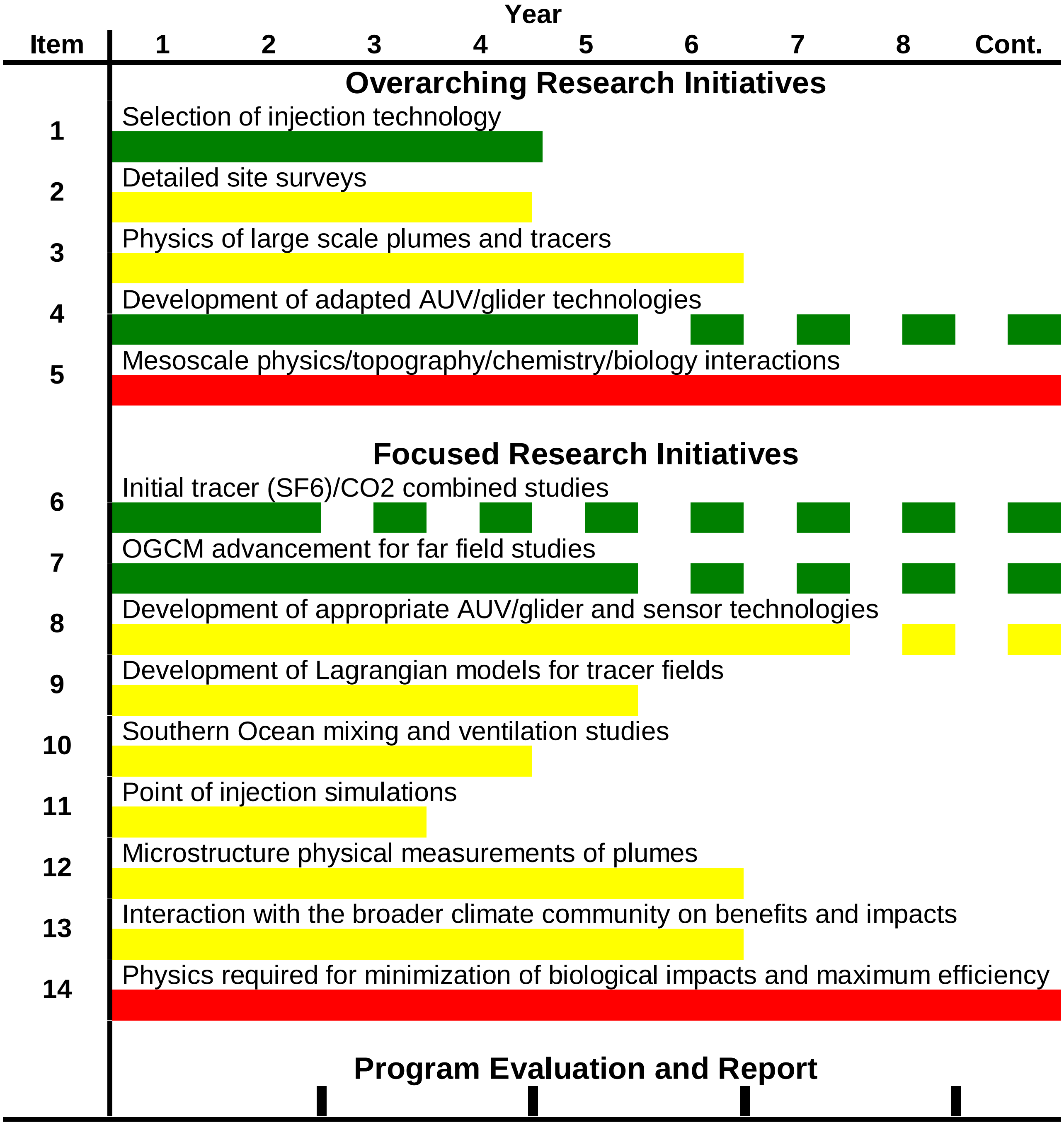

Biological Research Priorities for Ocean Carbon Sequestration

Summary: **Biological studies of the impacts of introduction of large quantities of CO_2 into the deep ocean must take into account the already massive penetration of fossil fuel CO_2 into the biologically rich surface ocean waters. Many deep sea animals have slower metabolic rates, and are adapted to a stable pH environment. The physiological cost of responding to changes in external pH has to be evaluated, and while acute pH changes close by a release point will clearly have impact it is the more subtle, but possibly more widespread, effects that are of primary interest.**

Background

Purposeful direct injection of CO_2 into the deep ocean may have significant influences on the structure and dynamics of deep-sea marine ecosystems. Such effects will depend on spatial and temporal scales of perturbation, and upon the absolute pH levels and CO_2 concentrations in the perturbed area (Auerbach et al., 1997; Caulfield et al., 1997). Changes in deep-sea ecosystems will arise through direct lethal and sub-lethal physiological effects on individual species or groups, with cascading indirect consequences for taxa not directly affected. These indirect effects could occur through altered trophic pathways, through biological interactions, or possibly through shifts in the amounts or sources of energy flowing from the upper ocean to the abyssal sea floor.

Organisms exposed to injection plumes with elevated concentrations of CO_2 (hypercapnia) and the associated pH reduction will respond with physiological repertoires that have evolved over thousands of generations. Although our knowledge of these repertoires is very limited for both shallow and deep-sea species, it is expected that the scope of tolerance to changes in seawater chemistry will be related to the level of environmental variability under which organisms have evolved. Because the physical characteristics of deep-sea habitats are stable over large areas and long periods compared to shallow water habitats, species inhabiting the deep-sea may exhibit greater sensitivity to a variety of environmental perturbations, including those associated with CO_2 injection. For example, the range of natural pH variation observed today in the upper ocean (0 to 1000 m) is fairly wide among ocean basins. The observed ranges are 0.25 pH units [Southern Ocean] to 1.0 pH units [Northeastern Pacific]). This may be compared to the narrow range of pH variability found in waters greater than 3000 m (0.1 to 0.2 pH units for the North Atlantic and North Pacific, respectively (Figure 1). This is already changing due to the large-scale invasion of fossil fuel CO_2 introduced by air-sea exchange processes (Brewer, 1978; Gruber et al., 1996).

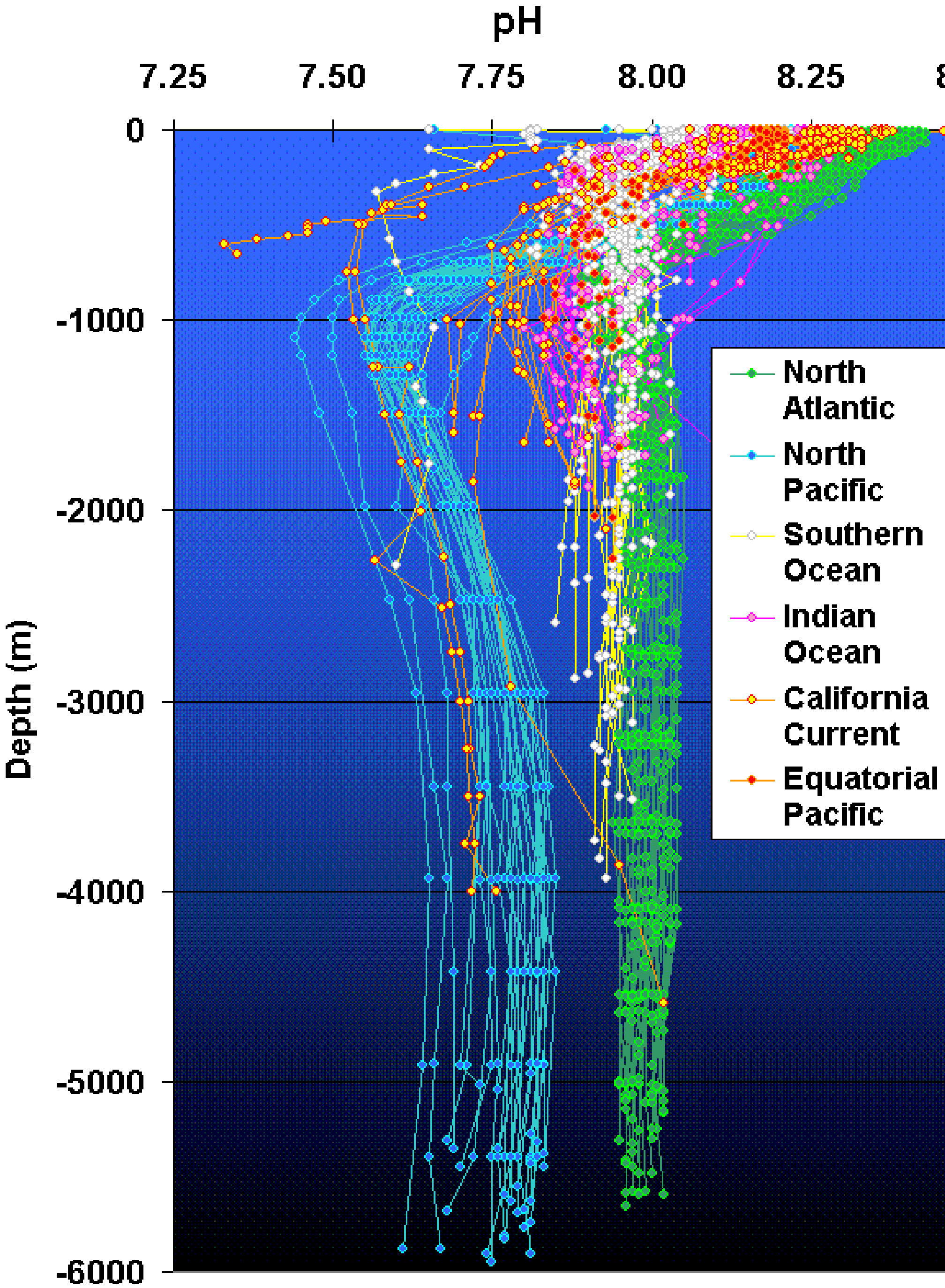

Figure 1. Global variation in the depth distribution of pH in several ocean basins. Profile data were obtained from the National Ocean Data Center (NODC) database. Accuracy of pH data is not known.

Limited data suggest that effects of elevated carbon dioxide on the physiology of marine organisms may be minor compared to the effects of seawater acidification. In most organisms from shallow water studied to date, reduced pH imparts physiological stress by reducing the binding efficiency of respiratory proteins (respiratory stress) and modifying the acid-base balance of internal fluids and tissues (acidosis). Organisms generally cope with acidosis by buffering internal pH levels, using enzymes adapted for ion exchange to restore acid/base balance (pH compensation). If internal pH changes can be restored to normal levels, reduced respiratory stress is also expected. Upon immersion in acidified seawater, organisms will range in response from indifference to decreased metabolic function to death, depending upon the level of stress and their compensation potential.

The effects of environmental pH reduction on many marine organisms are comparable to exercise-based tissue acidosis for species that undergo high levels of anaerobic activity. For example, sustained burst swimming by large predatory fishes (e.g. trout) causes tissue acidosis, so such fishes are often well adapted physiologically for high levels of pH compensation. The few data available suggest that the capacity for pH compensation of shallow-dwelling marine species, especially highly active species, is greater than that of deep-sea species. Predators in deep water, as well as their prey, tend to be less active; as a consequence, they have lower buffering capacity, lower metabolic rates, and lower concentrations of ion-regulating enzymes than their counterparts in shallow water. In summary, the capacity of organisms to tolerate pH changes caused by environmental acidification is expected to be linked, at least partially, with their buffering capacity and concentrations or activities of enzymes involved in proton regulation and exchange.

Responses of deep or shallow living marine organisms to hypercapnia are known poorly, and have been examined independently of the effects of pH changes only rarely. Some evidence suggests that hypercapnia, and not acidosis, induces a state or torpor or metabolic depression in at least some marine species, at least at low oxygen tensions (Portner and Reipschlager, 1996). Preliminary information on fishes (Kita et al. 2000) shows that CO_2 and pH might have different effects on survival under some circumstances. Even though the impacts of reduced pH associated with CO_2 injection are expected to be more severe than those caused by hypercapnia, this possibility has not been investigated. Moreover, if anticipated increases in CO_2 levels result in metabolic depression for a variety of taxa, it disrupt the population dynamics of species by reducing rates of individual growth and reproduction, even without any change in individual survival. It is therefore important to evaluate carefully the different, but potentially important impacts of pH and $CO_{2.}$

Prokaryotic marine microbes (Bacteria and Archaea) that live in the water column must deal immediately with metabolic consequences of acidification. They cannot swim fast enough to escape from the scales of environmental alteration proposed. Furthermore, their cell membranes are directly exposed to the proton concentration of the environment. Because they generate ATP using a proton motive force, a significant shift in environmental pH may make it more difficult to sustain a typical cytoplasmic pH (slightly alkaline) under conditions of energy limitation. Microorganisms adapted to life at circum-neutral external pH achieve a significant fraction of their proton motive force by establishing gradients of ions other than protons. As external pH values grade toward pH 6 these other ion motive forces will contribute less to the energy generating capacity of cells, i.e. all of this highly evolved energetic machinery may become a “genetic load”. A very different situation will prevail for deeper-dwelling sediment microbes at least in organic-rich settings. The activities of sulfate-reducing bacteria in the upper sediment regions can generate enough alkalinity to protect their own and deeper microbial populations as long as sulfate does not become diffusion-limited. For the most surficial microbial populations and deep-sediment populations in more oligotrophic settings, the pH problems will be intermediate between those faced by water-column populations vs. eutrophic-sediment populations.

Although investigation of the potential ecological consequences of large-scale direct ocean CO_2 injection is challenging owing to the complexity of ocean ecosystems, and the logistical difficulties of deep-sea research, much progress can be made by determining the direct effects of pH and CO_2 changes on the survival and metabolic performance of deep-sea species. Comparisons of physiological tolerance between deep and shallow marine species, among taxonomically divergent groups (e.g. predatory fishes, crustaceans and cephalopods versus gelatinous groups) and taxa important in energy flow may allow a first-order approximation of ecosystem consequences associated with direct CO_2 injection.

If deep-ocean CO_2 sequestration proves to be a viable option for carbon disposal, the depth of injection will depend on physical chemistry of the liquid CO_2 and on predictions of retention efficiency and plume dispersal based on physical oceanographic models. At present, 3000m appears to be a likely target depth. It is also important to consider the distributions of marine organisms as a function of depth. A very common pattern of distribution for sea floor organisms that has been observed repeatedly in various taxa, and in several parts of the world, takes the form of a bell-shaped curve in which the diversity of species is relatively low on the shallow slope and the abyssal plain, but peaks on the lower slope and continental rise. This pattern has been documented most thoroughly by Rex (1981), who showed peak diversity between 2000 and 3000m for polychaetes, protobranch bivalves, gastropods, cumaceans, invertebrate megafauna and fishes. Box core studies off the east coast of the U.S. showed a diversity peak at 3000m off Cape Lookout, the deepest station sampled, but a peak at mid-slope depths of 1200-1600m at more northerly sites (Blake et al. 1985; Maciolek et al., 1987a,b). Peak diversity for benthic foraminiferans are greatest at deeper depths (3000 to 5000 m) in the western North Atlantic (Buzas and Gibson 1969). Vinogradova (1962), summarizing worldwide diversity patterns based on several decades of work by Soviet oceanographic vessels also showed a large peak at a depth of 3000m. There are, however, places in the Pacific where peak densities are found at much greater depths (Hessler and Jumars, 1974) and several studies of megafauna that show diversity peaks at mid-slope depths rather than on the lower slope and the continental rise

Patterns of diversity for pelagic organisms appear to differ from those inhabiting the sea floor. The number of midwater species generally increases with depth to 500-1000m in the mesopelagic zone. Kikuchi and Omori (1985) showed peak diversity between 600-1000m for pelagic shrimps at two locations off the Pacific coast of Japan. Species richness of planktonic ostracods along 20ºW in the north-eastern Atlantic showed that maximum richness was consistently between 500-1000m and that the reduction in species richness at latitudes more than 40ºN was expressed throughout the water column (Angel, 1991). Below this mesopelagic peak, diversity decreases continuously with depth until near the sea floor, where it rises immediately above the sea bed (Omori et al., 1996).

It should also be noted that these patterns of increasing richness with depth apply only to diversity, not to total numbers of individuals or to biomass, both parameters that tend to peak higher on the continental slope (e.g., Maciolek et al., 1987) or in shallower waters.

Clearly these patterns should be examined more carefully at a regional scale once specific injections sites have been proposed.

Estimates of ecological consequences for deep-ocean ecosystems in various ocean basins can be considered in terms of the benefits and trade-offs associated with other carbon management scenarios. Although direct ocean CO_2 injection is expected to have negative consequences on deep-sea ecosystems in terms of changes in the abundance and diversity of deep-sea organisms, the magnitude of impacts are presently not known and very difficult to predict. Research is required in order to resolve, at least partially, changes in the structure and function of deep-sea ecosystems anticipated in association with CO_2 injection and to estimate the net benefit of sequestration scenarios in the context of global consequences of rapidly increasing atmospheric CO_2.

Biological Impacts: Research approaches

Irrespective of the method and depth (i.e. mid-water or sea floor lake) of direct carbon dioxide injection, there is a high potential for mortality of midwater or benthic animals, at least in the region near the outflow nozzle, and of sublethal, yet significant, impacts on the population survival of many species over even wider areas. Predictions of the scale of these biological impacts rely on realistic estimates of the spatial scales and range of perturbations to seawater chemistry associated with any direct CO_2 injection scenario. Therefore, the design of any ensuing biological program requires input from chemists, physicists and industry at the outset, concerning: 1) the expected distributions of CO_2 concentration and pH in three dimensions around the discharge sites, and 2) the kinds and amounts of contaminants that will be contained in CO_2 collected for ocean injection.

Species, population, and community consequences of CO_2 injection

Ideally, biological responses to elevated CO_2 and reduced pH should be studied at multiple levels of integration, including species, population, community and ecosystem. It is especially desirable to predict with realistic and testable models any CO_2-related changes expected at community and ecosystem levels where even small changes in species composition, diversity or dominance hierarchies could influence multiple species linked ecologically through trophic and competitive interactions. Testing and refinement of such models would require knowledge of species interactions and indirect effects that could only be determined with great expense, time and difficulty in sea floor communities, and which are virtually intractable problems in the bathypelagic realm.

Two alternative approaches could be employed to evaluate, with differing levels of certainty, the biological consequences of direct CO_2 injection on ocean ecosystems:

1) A comprehensive research program to determine the structure (distribution and abundance of species) and function (biological and energetic relationships among species) of deep-sea ecosystems and any modification of these patterns related to CO_2 injection,

2) A narrowly focused research program to determine the influence of pH and CO_2 perturbations on the survival and metabolic performance of a few metazoan and microbial groups representative of deep-ocean ecosystems.

The first approach, which is the most desirable from an environmental standpoint, would establish a very large scale, well-funded effort to understand processes that structure deep-sea non-chemosynthetic communities and ecosystems. Such a program would involve a large portion of the deep-sea research community over many years. This research effort should focus not only on the flow of materials and energy, but also on structuring forces at the community level (predation, competition, facilitation, etc.) and demographic factors that control important component populations (recruitment, life-history biology, mortality schedules, etc.). A program of this magnitude would yield highly relevant information concerning effects of various carbon management scenarios, while providing a quantum advance in our overall understanding of the global ecosystem. It is beyond the scope of this workshop to explore sufficiently the level of effort, methodologies, and high priority research activities required for the success of such a program.

The alternative approach would focus on key physiological and metabolic limitations of deep-sea organisms with respect to CO_2 injection. Such a program, which could begin immediately with a lower funding commitment, would provide information about impacts at the levels of individual metazoan species and bacterial functional groups. This approach will not provide reasonable input for ecosystem-level models of large-scale effects, but may allow coarse projections of changes in the abundance and diversity of species in impacted regions. Nevertheless, it is deemed prudent to initiate immediately research approaches that are both important and immediately tractable.

The important yet tractable questions differ somewhat between metazoans and microbes. Metazoans (multicellular animals from sponges to whales) can be identified and studied as distinct taxonomic species, whereas microbes, with few exceptions, cannot. For this reason, the emphasis in microbial ecology is on functional groups of organisms that control cycling of Carbon, Nitrogen, Oxygen and Sulfur in marine ecosystems, whereas the focus in metazoan biology is on representative species. Methodology and questions vary sufficiently between these two major groups of organisms that research priorities will be discussed separately.

Tractable Research Priorities: Metazoa

The highest priority of the research program should be to study the effects of pH and CO_2 on a small number of representative deep-sea species (3000m) as well as closely related analog species from depths shallower than 1500m. Species occupying the shallower depths have an evolutionary history that exposed them to pH variations associated with oxygen minimum zones and are therefore hypothesized to be more tolerant of low pH than species that evolved at depths where pH excursions are virtually non-existent.

Three variables most important in species-level comparisons with metazoans are mortality, metabolic rate, and sub-lethal effects on reproduction. These effects should be measured at a range of pH and CO_2 concentrations down to pH 6 to determine threshold responses. Mortality curves can be used to compute LC-50 values, which are useful for inter-specific comparisons within and between habitats. The reproductive parameters are important to measure because sub-lethal effects can potentially cause the extinction of species even when survivorship at the individual level is high. This occurs under conditions of stress when metabolic demands for maintenance consume all available energy leaving no energy to reproduce. The life histories of most marine metazoans include a dispersive larval phase that undergoes a dramatic metamorphosis into juvenile and adult phases. Because the survival of the population depends upon the survival of each life history stage, it is important to assess the sensitivity of larvae and adults to CO_2 and pH changes, when possible.

Investigation of the independent affects of CO_2 and pH changes is a high priority owing to the logistic difficulties of simulating CO_2 injection in small-scale experiments in the deep-sea. Containment, transport and release of CO_2 in the deep-sea are difficult using research ROVs and manned submersibles, thereby limiting the duration and spatial scale of small experiments, especially in pelagic environments. Acid injections (e.g. HCl or H_2SO_4) are much easier to perform in the deep-sea, and result in changes in seawater chemistry very similar to those produced by CO_2 injection down to pH 7.0, due to partial buffering by the seawater carbonate system (Figure 2).

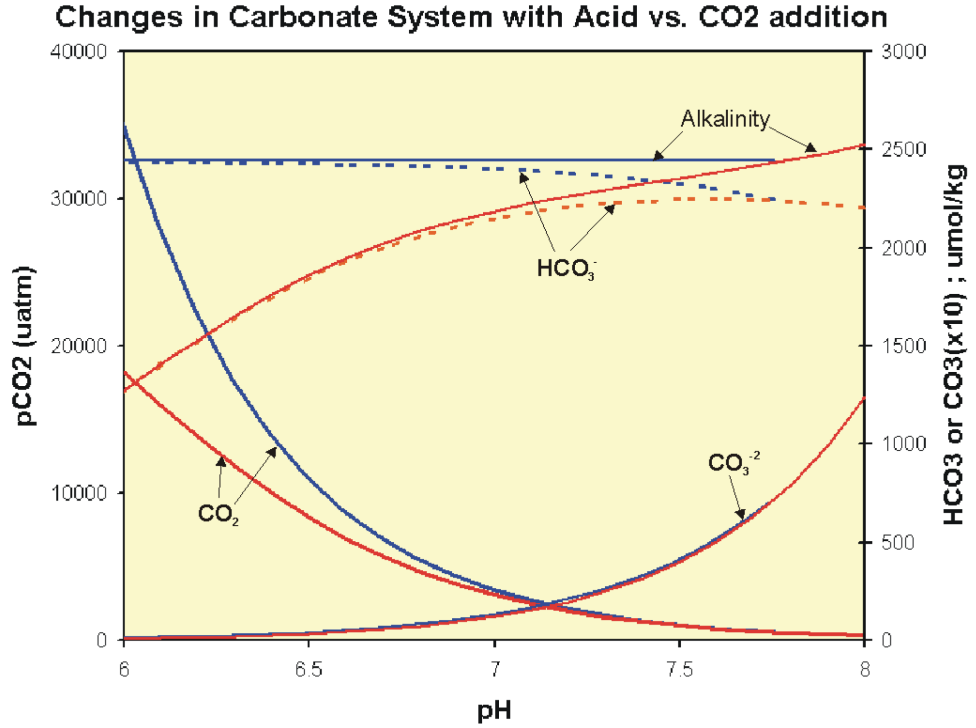

Figure 2. Changes in seawater carbonate chemistry caused by the addition of acid or carbon dioxide. Blue lines indicate changes in CO_2, HCO_3^-, CO_3^{-2}, and total alkalinity in relation to pH when CO_2 is added to seawater. Red lines indicate changes in these parameters when acid, rather than CO_2 is added. Total alkalinity, HCO_3^-, and CO_3^{-2} are indicated in the right y-axis. CO_3^{-2} concentrations are multiplied by 10x. Note that down to near pH 7.0, changes in seawater chemistry due to either acid or CO_2 injection are very similar.

For at least a limited range of pH perturbation, acid injections may simplify experimental manipulations on the sea floor and in the laboratory. Because low ambient bicarbonate concentrations may facilitate pH compensation for some animals (Portner and Reipschlager 1996), the reduction in bicarbonate levels resulting from acid injection must also be considered before using this method to simulate CO_2 injection. For pH reductions below 7.0 units, acid and CO_2 injections result in diverging ionic strengths of CO_2, H^+, and HCO_3^- (as well as alkalinity and total CO_2). It is important to understand the independent effects of CO_2, pH, and possibly other ions, on deep-sea organisms before substituting acid release for CO_2 injections. However, if it can be shown that pH is a good surrogate for the ensemble of CO_2 effects in deep-water species, or that risks associated with pH reduction are significantly greater than hypercapnia alone, then certain kinds of *in situ* experiments can be more easily conducted by dosing regions or enclosures with acid rather than CO_2.

Likewise, if it is shown that certain shallow-water species respond to CO_2 in a manner similar to that of deep-sea animals, then laboratory experiments can be logistically simplified by using the shallower dwelling species as experimental models. Virtually all animals studied to date that live below 1500-2000m are intolerant of reduced hydrostatic pressures and must, therefore, be studied either in pressurized vessels or in their natural environments. This requirement greatly complicates the design and execution of experiments, particularly long-term experiments, which will be required for studies of sublethal effects. It should therefore be a high priority to seek suitable experimental models from moderate depths.

Impacts from CO_2 sequestration must be investigated in a wide range of invertebrate and vertebrate animals from both mid-water and benthic environments. Although it is desirable to perform fundamental tolerance tests on as many species as possible from many phyla, certain groups which are particularly important because of their quantitative role in carbon cycling, their numerical abundance or diversity, and their probable sensitivity to chemical perturbations should receive the initial focus. The committee identified the following groups as being particularly important or tractable to study:

1. Gelatinous midwater organisms such as siphonophores, medusae, ctenophores and salps. This group can be tremendously abundant in certain mid-water zones, but is somewhat less understood than animals that can be collected more easily. Most gelatinous plankton have limited locomotory abilities compared to fishes, crustaceans, and cephalopods, and thus generally have low metabolic rates, and presumably narrower physiological scope for pH compensation. Moreover, because many of the cnidarian jellys are large and predatory, there is a high likelihood that they may be keystone predators in mid-water systems.

2. Copepods, must be included in tests of physiological tolerance because of their high numerical abundance in the plankton and because their fecal pellets are important vehicles for transporting small particles (i.e. carbon transport) rapidly into deeper water.

3. Echinoderms are important benthic animals to study because they constitute the most abundant deep-sea megafauna and because the calcareous endoskeletons found in many echinoderms might be affected adversely by drops in pH. Sea cucumbers, a common echinoderm group that lacks calcareous endoskeletons, are particularly abundant on the abyssal sea floor and probably process a large proportion

of the carbon that reaches the bottom from the overlying water column. During the course of their feeding activities, these animals rework the sediment continuously, probably having an important effect on the structure and stability of benthic infaunal communities.

4. Polychaetes, which are among the most diverse and abundant infaunal organisms in both shallow and deep systems, may be particularly suitable animals for experimentation because of their small size and numerical abundance.

5. Molluscs, including pteropods and heteropods in mid water and gastropods and bivalves on the sea floor are appropriate models for pH studies because of their calcareous shells. Gastropods are among the most diverse of deep-sea animals and are known to reach a diversity peak in the Atlantic around 3000m, which is a target depth for CO_2 sequestration.

6. Amphipods are abundant scavengers on the sea floor at both slope and abyssal depths. In past studies, they have been trapped in baited pressure vessels and transported to the surface without depressurization for experiments. This logistical advantage makes them an experimental model of choice.

7. Fishes from the deep sea are important animals to consider, but very sensitive to pressure changes, making them difficult to work with in the laboratory. A few species of mid-water fishes from bathypelagic depths have been successfully maintained for a few days and these should be considered as initial models for tolerance studies.

In addition to these metazoan models, it is vitally important to examine pH and CO_2 effects on foraminiferan protozoans. These microscopic organisms, which are probably responsible for large amounts of carbon flux and are abundant in both mid-water and benthic habitats, have very delicate calcareous shells that are likely to be affected by reductions in pH.

Small-scale field experiments represent a tractable supplementary approach that will provide certain kinds of information that cannot be obtained in the laboratory. The technology already exists for injecting small quantities of liquid CO_2 on the sea floor (Brewer et al., 1999). This technology can be exploited to good advantage in experiments designed to investigate the plume effects on benthic infaunal communities, the responses of mobile organisms to CO_2 pools, and the possibility that scavengers might be attracted to areas where CO_2 has caused mortality of other organisms.

It should be noted that other kinds of field experiments are possible. These include mesocosms (enclosures containing natural marine communities, either moored in mid-water or on the bottom) and large-scale releases of CO_2 in the natural environment. Mesocosms have been used successfully in surface waters where they may be opened to the atmosphere. However, in deep-water, where they would have to be sealed completely from the surrounding water masses in order to contain the animals and properly control the chemical environment, they would be less useful, at least for studies involving metazoan animals. Mid-water mesocosms would be impractical because of low animal densities. Large-scale (i.e. >50 m^3 liquid CO_2) release experiments are planned for studies of plum dispersal and could be useful for biological studies under some circumstances, as long as the experiments are replicated or proper attention is paid to statistical rigor in an unreplicated design. The issues involved with such large-scale experiments are beyond the scope of the present discussion

In summary, the following tractable approaches are recommended as priorities for studies of metazoan animals:

1. Determine mortality curves (LC-50 values) and metabolic rates of abyssal and bathyal animals from a wide variety of representative taxonomic groups at a range of pH values and CO_2 concentrations.
2. Experimentally investigate sublethal effects on deep-sea animals, focusing particularly on effects that might reduce the capacity for reproduction.

3. Using small-scale experiments on the sea floor, investigate community responses of infauna to plumes of CO_2 and acidified seawater.

4. Using small-scale experiments on the sea floor, investigate the behavior and survival of motile megafaunal organisms in response to CO_2 and acidified seawater.

Tractable Research Priorities: microbes

The first-order questions about the microbiological impacts of carbon dioxide sequestration in the ocean (in contrast to questions about impact on metazoans, which are aimed at anticipating possible differential response of different taxonomic groups) must focus on impacts of disposal on diverse microbiological transformations of carbon, nitrogen, sulfur and oxygen. These transformations form the basis for fundamental biogeochemical cycles, which must remain intact in marine ecosystems. It is microbiological dogma that only a small fraction of naturally occurring Bacteria and Archaea are represented in culture collections. Since it is often difficult to assign metabolic motifs or ecological niches to uncultivated prokaryotes (e.g. characterized only by ribosomal RNA signatures), a focus on loss of ecosystem function in response to elevated concentration of CO_2 must target breakdown of microbial processes rather than loss of species. Because disposal sites may be in midwater, at the ocean floor or even in deep anoxic basins, this broadens the suite of transformations that should be considered. Shallow and deep (ca 3 km) natural microbial populations can be studied with equal ease since pressure-requiring bacteria have only been isolated from much greater depths. Experimental microcosms (water only and sediment-water interface types) should yield considerable useful data because the microbial populations enclosed will be large. In some cases bacteria believed to be representative of those performing significant portions of natural biogeochemical cycles be tested for carbon dioxide and pH effects in pure cultures.

The perturbations to be studied range from a few tenths to approximately 2.0 pH units (from 8 to 6). The former represents the predicted short-term impact of our current accelerating rate of CO_2 release. This emphasizes the need to study ocean surface microbial populations as well, since they will be impacted in the future even in the absence of a decision to go ahead with purposeful sequestration. The 2.0 unit change seems to be the most drastic predicted by current simulation models, and it is achieved only as conditions approach carbon dioxide saturation. Initially, simple acidification with inorganic acids and enhancement of carbon dioxide content will be tested separately to determine are any differential effects on microbial processes. For example, known oceanic bacteria that oxidize hydrogen sulfide at mesophilic temperatures are typically inhibited by their own acid production at pH values greater than 6.0. It is assumed, due to the high sulfate content of seawater, that this is a pH effect *per se* and not a matter of end product inhibition. Even mesophilic sulfide-oxidizing bacteria isolated from vent environments (which are some of the most acidic regimes found in marine ecosystems) are significantly inhibited by pH values possible with direct injection. For example, *Thiomicrospira crunogena* is 60% inhibited, relative to its optimum, by a pH as low as 6.0 (Ruby and Jannasch, 1982). Other sulfide-oxidizing, surface-dwelling bacteria that are known to achieve high densities in eutrophic sediments generate acidity by their metabolism but a pH depression of 0.5 units (e.g. from 8.2 to 7.7) is the maximum that has been observed (Nelson et al., 1986). It is therefore assumed that values in the range of 7.5 to 6.0 are completely outside the evolutionary experience of these microbes.

If a CO_2-produced pH value approaching 6.5 or 6.0 also inhibits oxidation of hydrogen sulfide this will have fundamental implications for sequestration in basins or near the sediment-water interface. The rationale is as follows: There will clearly be metazoan, and perhaps microbial, die-offs in response to local pH minima in the region of 6.0 or 6.5, e.g. near the point of discharge. The resultant decomposing organic matter at the sediment-water interface will fuel accelerated sulfate reduction in surficial sediments. If the resultant hydrogen sulfide cannot be oxidized by other microbial guilds until the pH is 7 or 7.5, then a potentially large hydrogen sulfide plume will join the carbon dioxide plume. Marine metazoans may be much more sensitive to hydrogen sulfide than to carbon dioxide.

Because there is a virtual absence of studies on the impacts of acidification on fundamental marine microbial processes, those transformations to be studied include:

1. Aerobic respiration of organic carbon. *In situ* concentrations of organics, as well as higher concentrations – mimicking what might happen with enhanced sediment microbial fermentation and release of organics to the overlying water – will be examined.

2. Grazing by nanoflagellates on bacteria at different pH and CO_2 values.
Microbial fermentation process in the sediments. Some of the resultant organic acids may begin to act as general decouplers of the microbial proton motive force as the external pH approaches 6.

3. Oxidation of reduced forms of nitrogen and sulfur (e.g. ammonia, nitrite, hydrogen sulfide, elemental sulfur and thiosulfate). The conversion of NH_3 to NH_4^+ is strongly pH dependent and may have implications for relative efficacy of nitrifying chemoautotrophs at pH 6 vs. pH 8.

4. Reduction of oxidized forms of N, S and C (sulfate → sulfide; nitrate → ammonia or dinitrogen gas; carbon dioxide → methane or acetate).
Simple measures of how microbial community structures change in response to a sustained pH change. Measures of community diversity and membership (e.g. denaturing gradient gel electrophoresis) or population levels/activity (e.g. DNA/RNA ratios) may be employed.

In addition to the named molecular methods, techniques employed might include use of radiotracers (^{35}S, ^{14}C), wet chemistry (oxygen uptake, ammonia production), gas chromatography, standing crops of cells (epifluorescence microscopy, ATP), stable isotope signatures (changes in dominant pathways of carbon dioxide fixation or breakdown).

It should also be possible to use known techniques to analyze several of these microbial transformations in pilot-scale CO_2 release experiments, especially if the release is confined near the sea floor where ROV operation may be more straightforward.

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Projected Research Time Line and Difficulty Estimate									
Item	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Beyond**
	Overarching Research Initiatives								
1	Effects of CO2 perturbation on the survival of deep-sea organisms								
	🟩	🟩	🟩	🟩	🟩				
2	Sublethal effects of CO2 perturbation on the reproduction and population dynamics of deep-sea organisms								
	🟨	🟨	🟨	🟨	🟨	🟨	🟨		🟨
3	Comparison of biological sensitivities to CO2 among shallow, mid-depth, and deep-sea species								
	🟩	🟩	🟩	🟩	🟩		🟩		🟩
4	Ecosystem models evaluating population and community-level effects of CO2 sequestration								
			🟥	🟥	🟥	🟥	🟥	🟥	🟥
5	Microbial biogeochemical studies								
	🟩	🟩	🟩	🟩	🟩	🟩		🟩	
	Specific Research Foci								
	Metazoan animals								
1	Survivorship versus CO2 & pH dose for various taxa from shallow, mid-depth, and deep areas								
	🟩	🟩	🟩	🟩	🟩				
2	Degree of metabolic depression versus pH and CO2 exposure								
		🟨	🟨	🟨	🟨		🟨		🟨
3	Changes in reproductive output versus CO2 and pH exposure								
	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
4	Effects of pH, CO2 exposure on larval survival.								
		🟨	🟨	🟨	🟨	🟨		🟨	
5	Small scale in situ studies of infaunal animal responses to CO2 plumes								
	🟨	🟨	🟨	🟨					
6	Small scale in situ studies of the behavior and survival of mobile animals exposed to CO2 plumes								
		🟨	🟨	🟨	🟨		🟨		
	Microbial Process Studies								
7	Aerobic respiration of organic carbon versus CO2 levels								
	🟩	🟩	🟩	🟩	🟩	🟩			
8	Grazing by nanoflagellates on bacterial versus pH and CO2 levels								
	🟩	🟩	🟩	🟩	🟩	🟩	🟩		
9	Oxidation of reduced nitrogen and sulfur vs pH and CO2 levels								
		🟩	🟩	🟩	🟩	🟩		🟩	
10	Reduction of oxidized N, S, and C vs CO2.								
		🟩	🟩	🟩	🟩	🟩		🟩	
	Ecosystem Models								
11	Linked ecosystem / circulation models of population and community changes associated with various CO2 injection scenarios								
			🟥	🟥	🟥	🟥	🟥	🟥	🟥
12	**Program Evaluation and Report**								
	Key:	**Feasible**	🟩		**Challenging**	🟨	**Difficult**	🟥	

APPENDIX 1
ATTENDEE LIST

OCEAN CO_2 SEQUESTRATION MEETING
MBARI- DoE/NETL

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