Draft Workshop Report for Funding Sponsors
Carbon productivity responses to increased dissolved inorganic carbon concentrations in surface ocean: Exploring the feasibility of an *in situ* mesoscale carbon addition experiment.

Monday – Tuesday, 23-24 March 2009

A workshop to explore the scientific justification and logistical feasibility of an *in situ* open ocean mesoscale CO_2 perturbation experiment was held at Lamont-Doherty Earth Observatory at Columbia University (LDEO) on 23-24 March, 2009 in Palisades, New York (see Appendix I for agenda). The objective of the workshop was to assess the current understanding of the potential effects on open ocean ecosystems and biogeochemical cycling resulting from CO_2 increases in ocean in response to increased atmospheric pCO_2 and to determine the feasibility of an *in situ* open ocean mesoscale CO_2 perturbation experiment. Support was provided by three sources: 1) LDEO Climate Center; 2) LDEO Advisory Board Innovation Fund; and 3) NSF – ADVANCE of the Earth Institute at Columbia University. Approximately 15 people attended over the course of the two meeting days. Participants included both LDEO and outside scientists representing the fields of modeling and physical, geochemical and biological oceanography (see Appendix II for participant list). The meeting format was interactive and strong on discussions and calculations. Products of the meeting included: 1) scientific justification of a large scale open ocean experiment 2) a vision of a semi-enclosed experimental design; 3) prioritization of two potential experimental locations along with justifications for each site; 4) anticipated biological and geochemical responses; 5) appropriate observations and measurements necessary to document experimental responses.

Serendipitously, this workshop lent itself to providing a brief overview of conclusions to be presented at an International SOLAS meeting later that week where several representatives of major US funding agencies were present (see Appendix III for presentation slides). Timely, influential feedback is expected. To further communicate the results of the meeting, versions of this report are planned to be submitted to appropriate outlets such as *EOS Transactions, AGU* - Meeting Reports section and *The Oceanography Society Magazine* (Dec. 2009 special issue) and distributed to mailing lists of Ocean Carbon Biogeochemistry (OCB) and Surface Ocean Lower Atmosphere Study (SOLAS).

In situ eddy-scale open ocean mesoscale amendment experiment

The workshop began with a discussion of a true *in situ* open ocean carbonate chemistry perturbation experiment which would be scientifically valuable for testing effects on open ocean ecosystems and biogeochemical cycling of surface ocean CO_2 increases in response to the atmospheric pCO_2 increase. It was concluded that, although such an experiment could be accomplished, the resources required to set up and maintain an eddy-scale pCO_2 perturbation experimental site would require extraordinary funding amounts perhaps on the order of a National Science Foundation Long Term Ecological

Research site (~multiple $10's of millions) The group agreed to spend the workshop time developing an alternative experimental approach which could be accomplished within the framework of traditional (even if large-scale) funding schemes and would represent an improvement on past experiments.

Alternatives to *in situ* eddy-scale open ocean mesoscale amendment experiment

Several alternatives to a full-scale *in situ* experiment were discussed: 1) very small-scale *in situ* open ocean perturbations; 2) natural CO_2 gradients (spatial or temporal); 3) closed-system mesocosms; 4) large (semi-enclosed) "maricorrals," a term we derived from limnological experimental containment systems called "limnocorrals." The merits and drawbacks of each were continually revisited as ideas progressed. By the end of the workshop it was generally agreed that multiple large maricorrals were the preferred method. Preliminary engineering and design concerns were addressed and are discussed further in the next section. Shortcomings of the very small (i.e. 1 km^2) *in situ* open ocean amendments were first, the very fast diffusion and dispersion of the patch and second, the fact that the patch would be very difficult to track after manipulation. It was demonstrated that the natural amplitude in seasonal and latitudinal gradients of pH and pCO_2 was on the same order as the predicted global average change due to anthropogenic forcing. Exploiting these natural CO_2 gradient systems such as coastal upwelling plumes, latitudinal differences or seasonal cycling for the purpose of testing direct effects of carbon availability and pH, would be highly challenging. Separating out the effects of CO_2 from confounding factors would be difficult because the CO_2 change in these environments occurs contemporarily with many other changes in biological community structure, biogeochemistry and physical hydrography. Closed-system mesocosms were generally not favored because of well-known "bottle effects" where conditions within a control bottle are distorted from the ambient environment. It was noted that mesocosms would require some level of manipulation (i.e. nutrient amendments or chemostat) which could mask ecosystem level, but perhaps subtle, interactive effects of a CO_2 treatment. However, the utility of mesocosms for multiple treatments or replicates was acknowledged.

Open ocean maricorrals

Size, construction qualities, deployment strategies, amount of acid or CO_2 necessary to perturb and time necessary to perturb were discussed with some aspects better resolved than others.

In an effort to preserve the theoretical desirability of an *in situ* experiment but reduce the logistical challenges of patch dilution and shear, a semi-enclosed maricorral structure was envisioned. Maricorrals would need to be "large" to minimize container effects (e.g. potential biofouling, shading, small scale turbulence), maximize sampling volume and be inclusive of higher trophic levels. They would be open at the top to allow for "natural" atmospheric and optical conditions. An open bottom would take advantage of natural diffusive nutrient fluxes and vertically migrating zooplankton grazers, but would also dilute the perturbed water. The circumference would be walled as a way to slow advection and diffusion of the amended water. An important issue left unresolved was whether the curtain walls would necessarily have to be made of an impermeable material (i.e. a "shower curtain") or whether an open net of some calculated mesh size could serve to provide a balance between resisting deformation from shear versus slowing advection of the perturbed water by breaking up the energy length scale. The depth of the curtain wall theoretically should be equal to or below the depth of the mixed layer where the perturbation was achieved and at or just beyond the thermocline.

Figure 1: Website photos representing large, open ocean mariculture structures which could conceivably be modified into experimental maricorrals.

Industries such as commercial fishing and oil containment have expertise in deploying large scale equipment in the surface open ocean (Fig. 1). To minimize "reinventing the wheel," the design, engineering and possibly even the deployment of maricorral structures might be more efficiently accomplished by partnering with industry.

It was calculated that for a 100 m diameter x 25 m deep enclosure which is the nominal size of tuna pens (see Fig. 1), about 1000 kg of H_2SO_4 would be needed to achieve a reduction of 0.2 pH units plus associated shifts in carbonate chemistry or about 27 cylinders (1000 kg) of compressed CO_2 would be needed to achieve a reduction of 0.2 pH units and an increase of about 100 μmol/kg in total CO_2 (DIC) plus other associated shifts in carbonate chemistry (See Table 1). These level of changes in pH and total CO_2 are about twice as large as the seasonal amplitude in present-day open ocean surface waters. This amount of H_2SO_4 or CO_2 could be added on timescales of about a day. The cost of the amendment substrate (acid or CO_2) would be small in relation to that of the entire experimental set up, therefore, multiple or repeat amendments could be considered.

Utilizing maricorrals would provide an additional benefit of multiple treatments or replicates. Two maricorrals are absolutely essential because the introduction of any structure requires at least one control and one treatment. Additional maricorrals would allow additional treatments. A design to test several gradients of perturbation was favored by many, although the redundancy of replicates was appreciated given the risks involved in open ocean research, not to mention natural variability.

Method of perturbation

The method of experimental perturbation of a water mass that would most closely mimic the effects of increased atmospheric pCO2 is the addition of CO_2 gas. A possible future increase of atmospheric pCO_2 from 350 to 600 μatm could only increase the total CO_2 concentration in the world's surface oceans on the order of about 5% or by 100 μmol/kg and decrease pH by about 0.2. Impacts on both organic and inorganic biological carbon production would be more likely due to the increase in pH and the relative equilibrium state of carbonate chemistry (the relative concentrations between dissolved CO_2, bicarbonate ions and carbonate ions) rather than the small absolute increase in total dissolved inorganic carbon (DIC) concentration. Acid addition would require much less mass than CO_2 injection to accomplish the same change in pH and carbonate equilibrium. For these reasons, it was determined that the logistical and financial benefits of using an acidification method to achieve a 0.2 change in pH and a ≈200 μatm change in pCO_2 was worth considering as a trade off from the cost of not generating the small absolute total CO_2 (DIC) concentration increase. The differences in response of the inorganic carbon system of a CO_2 addition compared to a pH change at two different temperatures are shown in Table 1. The major difference is that adding acid to change the pCO_2 does not lead to a change in total CO_2 (DIC) but rather decreases the carbonate concentration. Operationally, acidification would be accomplished by pumping seawater from the mixed layer, introducing concentrated acid to form moderately acidified seawater then returning the acidified seawater to the mixed-layer water column. Yet to be determined would be the optimal moderated pH and pumping rates to optimize fast deployment of the perturbation with stress-avoidance on the biological community. Inert tracer gases SF_6 and ^3He would be added so that the perturbed waters could be tracked through "leaky" maricorrals and gas exchange could be quantified. Speculating that a 1000:1 initial acid dilution might be acceptable, it was calculated that the time to acidify one maricorral would be about 1 day (100 gpm pump x 100 m diameter x 25 m deep at 1000:1 dilution of acid).

Table 1. Response of the inorganic carbon system to a CO_2 addition and acid addition corresponding to a pH change of 0.2.

Add	Salt	t(°C)	TA	pH	Total CO_2	pCO_2	HCO_3	CO_3	Re	Ωar
Initial	35	18	2300	8.1	2024	336	1817	196	10.1	3
CO_2	**35**	**18**	**2300**	**7.9**	**2123**	**577**	**1970**	**134**	**12.7**	**2.1**
Acid	**35**	**18**	**2195**	**7.9**	**2023**	**550**	**1877**	**128**	**12.5**	**2.0**
Initial	35	4	2300	8.1	2131	333	1991	123	13.4	1.8
CO_2	**35**	**4**	**2300**	**7.9**	**2206**	**556**	**2094**	**82**	**16.5**	**1.2**
Acid	**35**	**4**	**2224**	**7.9**	**2132**	**537**	**2024**	**79**	**16.4**	**1.2**

Add: addition method. Initial are the initial conditions. Following lines show the change due to either CO2 additions or acid addition for a temperature of 18oC (first 4 lines) or 4oC (last three lines). TA = total alkalinity; HCO3 = bicarbonate concentration (µmol kg-1); CO3 = carbonate concentration (µmol kg-1); Re = Revelle factor; Ωar = saturation state of aragonite. Calculations using the Excel worksheet of Pierrot coded after the program of Lewis and Wallace (http://cdiac.ornl.gov/oceans/co2rprt.html).

Legal, permitting and political considerations

In addition to the technical challenges, there may be legal (and political) challenges in intentionally acidifying a patch of ocean. Ocean "dumping" regulations as defined in London Convention and Protocol, as well as customary international law as reflected in the UNCLOS are currently being reviewed, and possibly regulated with respect to ocean "fertilization" studies. Difficulties in obtaining permits were brought up as a major concern for any future open ocean addition-type experiments, especially in light of the negative publicity surrounding the recent LOHAFeX project even though a CO_2 or acid addition is not expected to be a form of fertilization.

Optimal locations

Due to spatial variability of current global pCO_2 and CO_2 fluxes, the results of a CO_2 addition or acidification experiment would very likely vary in different locations (Fig. 2). Two major oceanic regions, the subtropical Pacific and the high latitude ocean, were prioritized as candidates for a CO_2 manipulation. Each region has specific characteristics useful for such a study.

The subtropical Pacific covers a large representative area of the global ocean. Warm water would produce faster physiological and community responses. Nitrogen fixers are present so predicted changes to N-fixation rates could be observed. Nutrients are generally recycled in the microbial loop so changes to nutrient availability (both macro and micronutrients) and the heterotrophic bacteria could be apparent. Long-term time-series data may benefit from a look back using these experimental results to identify potential ecosystem changes due to pCO_2 increases from earlier decades through the present. Open ocean conditions are relatively accessible from Hawaii.

Alternatively, high latitudes are important for the global redistribution of nutrients and trace elements. This is particularly true in water mass formation regions such as those associated with intermediate water formation. These regions are typically net sinks for carbon in the current ocean (Fig. 2) and important in the redistribution of nutrients. A high latitude location also would have more biomass and therefore likely produce more easily detectable geochemical response signals. Important calcifying organisms such as coccolithophorids and pteropods (Fig. 3) are present, so impacts on calcification rates could be observed. High latitude regions are predicted to have the earliest pH changes in response to anthropogenic forcing. They also have lower calcium carbonate saturation states and are expected to experience greater biological changes. There may be significant interactive effects on primary productivity with respect to pH and carbon availability along with known iron and light stress. Smaller quantities of amendments would be necessary to achieve target pH and carbonate equilibrium targets.

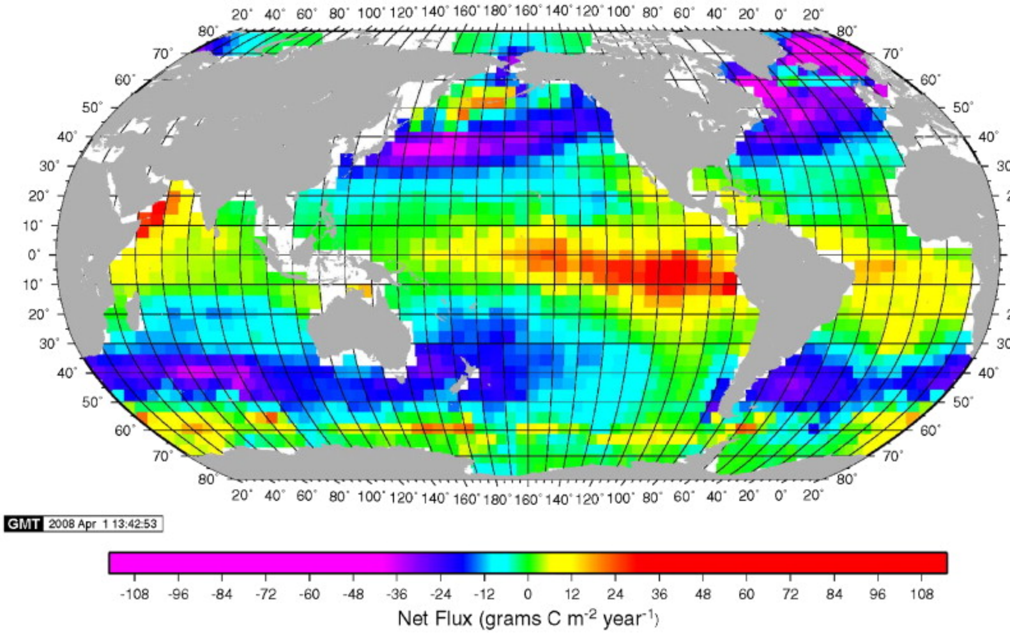


Figure 2 ***From Takahashi et al. 2009 Deep Sea Research II.*** **Climatological mean annual sea–air CO_2 flux (g-C m^{-2} yr^{-1}) for the reference year 2000 (non-El Niño conditions).**

Time scales and limitations

It was generally agreed that maricorral conditions could be maintained for a period on the order of weeks. As with *in situ* experiments, the length of time the patch can be maintained influences the level of responses that can be observed. The importance of the quantity and stoichiometry of exported particles was recognized as a key component of the biological pump and its influence in global biogeochemical cycles. However, because the biogeochemical responses are predicted to be subtle (see next section) rather than a bloom-like response experienced during iron fertilization experiments, detecting geochemical feedback signals or changes in export (either quantity or stoichiometry) may be difficult over this time period. Also noted were other effects that would not be tested by such an acidification or pCO_2 perturbation experiment. These include temperature effects, changes in meteorology and hydrography (e.g. winds, mixing depths, clouds), long-term adaptation of biological community and deep ocean geochemical feedbacks.

Predicted responses

A review of the current literature from laboratory and field experiments revealed many gaps in our current state of knowledge regarding likely changes to organisms due to pH and pCO_2 changes. However, some overall hypotheses about open ocean responses were formulated. It appears likely that changes in CO_2 availability will affect various phytoplankton functional groups in different ways, depending on the extent of their physiological plasticity. Groups that rely on passive diffusion of CO_2 may get a slight advantage. Groups which employ carbon concentrating mechanisms may reallocate cellular resources. Changes in uptake stoichiometry and elemental ratios of phytoplankton seem likely along with higher N-fixation rates and lower calcification rates. Some evidence of increased photosynthetic efficiency in culture experiments suggests possible responses in this parameter, especially at low light. Subtle changes in growth rates and changes to phytoplankton assemblages could be observed, however, a large bloom response is not expected. Direct effects to heterotrophic eukaryotes are unkown, but would likely be significant to calcifiers (i.e. pteropods [Fig. 3], foraminifera). Metazoans and fish larvae may also show sensitivity to pH but effects might not be observable in this experimental design. Indirect (trophic cascade) effects could change grazing patterns and affect the grazing community. Heterotrophic bacteria are often carbon limited in the surface ocean, so increases in C:N in primary producers would likely increase bacterial productivity and remineralization. Taken together, the interaction among these less-than-dramatic responses are predicted to have the cumulative effect of a significant restructuring of the trophic dynamics and accompanying biogeochemical feedbacks. It will be important to make measurements of fast-responding physiological and molecular responses because community restructuring and biogeochemical responses could take longer to develop than maricorral experimental conditions can be maintained. It is at this point where natural analogs could serve as models to predict these longer term developments based on observed changes in the phytoplankton and heterotrophic microbial community. In summary, we generally predict:

- Changes in elemental ratios
- Changes in assemblages, community, trophic relationships (bacterial, phytoplankton, zooplankton and higher)
- Higher N-fixation rates
- Lower calcification rates

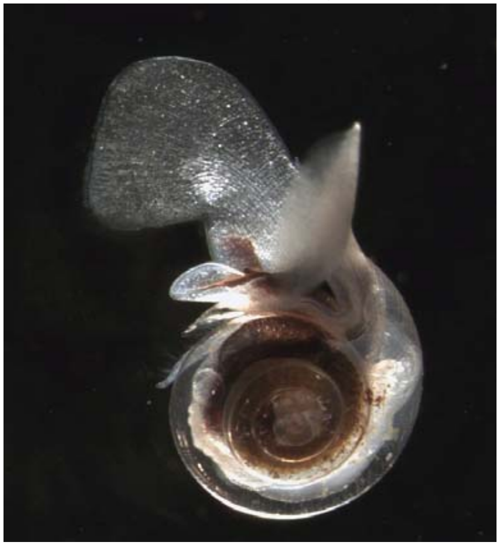


Figure 3: NOAA image of a pteropod

Measurements and observations

There are three major categories of observations necessary for a successful pCO_2 perturbation experiment: 1) those to monitor the geochemical experimental environment (i.e. chemical changes as a direct effect of lower pH and shift in carbonate equilibrium; 2) those which will target biological responses; 3) those which might detect changes in biogeochemistry due to feedback from the biological response. As usual, the answer to the question of what to measure was, “everything.” However, of course, platform space and time constraints would necessarily force some prioritization. Intensity and extent of measurements should of course match the expected pattern of the response. Some observations are more critical at early stages of the experiment while others will be more important later. Tactics for how to best sample multiple large maricorrals was briefly addressed, but no concrete conclusions came from discussions. The list below is not exhaustive:

Physics

Mixed layer depths; advection; vertical diffusion

Optics

Euphotic zone, light quality

Chemistry

Inorganic Carbon: At least 3: total CO_2; pCO_2 and total alkalinity

Major nutrients – including NH_4

Micronutrients – Fe, Co, Cu, Cd, Mn, Zn – concentrations; speciation not necessary for all – depends on location

Organic Chemistry: POC, PON, POP, DOC, DON, DOP

Inert tracers SF_6, ^3He

^{234}Th export? can we do in time frame?

Biology/Ecology

Carbon productivity – ^{14}C organic and inorganic fixation rates and allocation (lipids, carbohydrates, DOC excretion, etc.)

Photosynthetic efficiencies (Quantum yield of photosynthesis; photochemical efficiency (fv/fm)

Bacterial productivity

Molecular stress indicators, proteins concentrations, RNA, DNA

Size fractions

HPLC/fluorometric phytoplankton pigments

Flow cytometry

^{15}N uptake

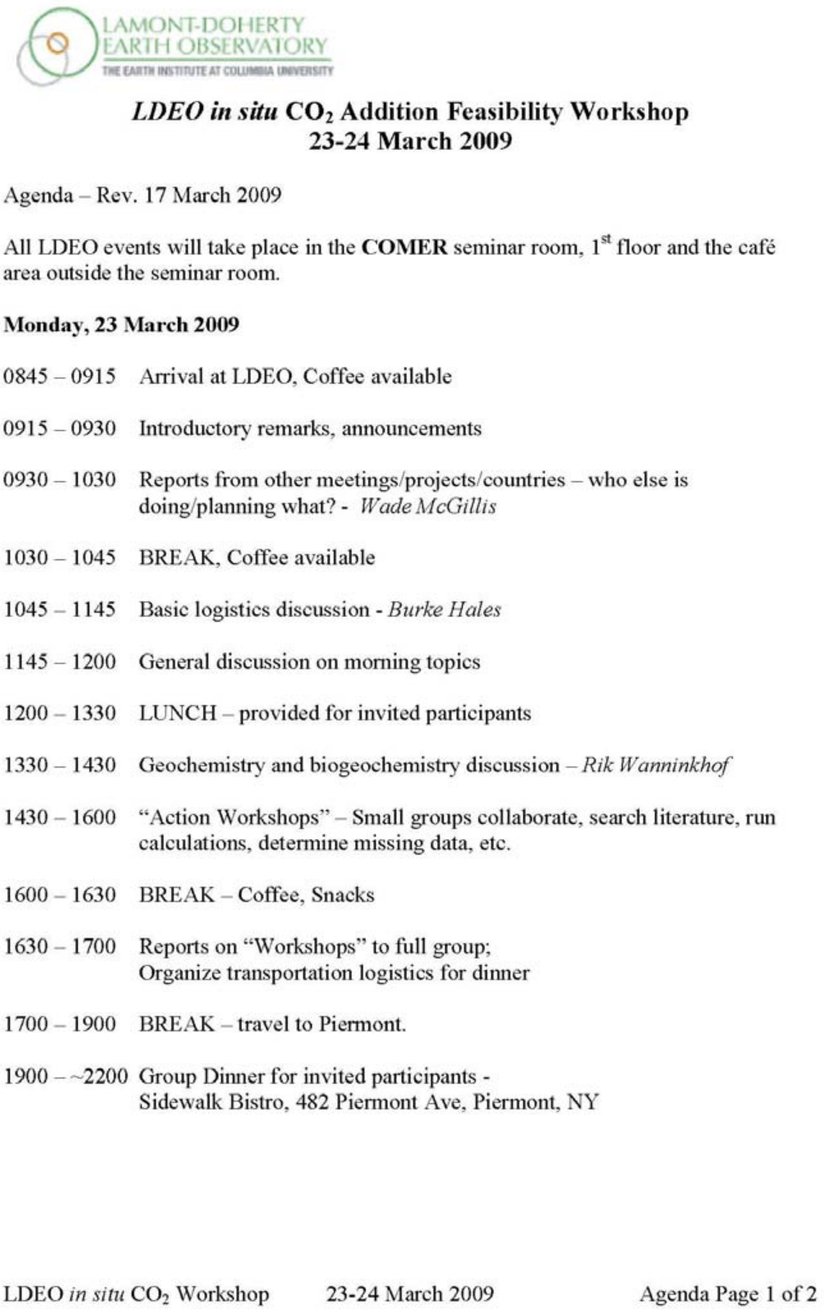
triple O_2 isotopes? ^{16}O, ^{17}O, ^{18}O

Grazing rates, grazer ID, grazer calcification rates

Modeling approaches

Generally, the biogeochemical models currently in use do not have mechanisms that would be responsive to observed experimental changes. It will be important to identify and quantitatively define energy and substrate trade-offs to organisms (i.e. calcification vs. growth; carbon-concentration vs. nutrient demands) in order to predict potential changes to communities in response to CO_2 perturbation over longer time scales. Complete intracellular models are not necessarily required for this approach. However, key intracellular mechanisms might be identified which significantly alter an organism's "traits and trade-offs" resulting in an environmental shift. Bridging scales from intracellular to global is a huge challenge for modeling, but this type of experiment could provide unique data in support of understanding effects of the large predicted increase of atmospheric pCO_2 on ocean ecosystems.

Appendix I
Agenda



LAMONT-DOHERTY
EARTH OBSERVATORY
THE EARTH INSTITUTE AT COLUMBIA UNIVERSITY

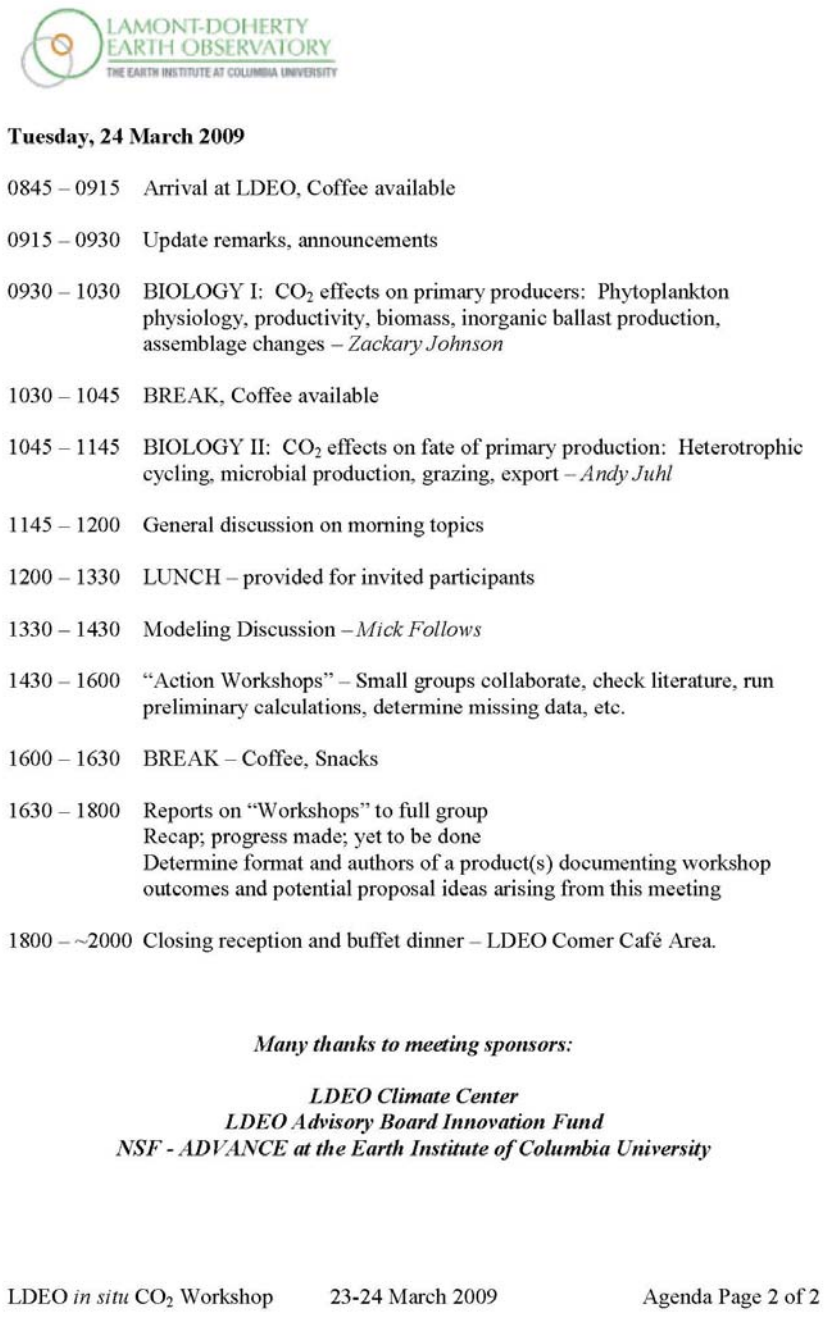
LDEO in situ CO_2 Addition Feasibility Workshop
23-24 March 2009

Agenda – Rev. 17 March 2009

All LDEO events will take place in the **COMER** seminar room, 1st floor and the café area outside the seminar room.

Monday, 23 March 2009

0845 – 0915	Arrival at LDEO, Coffee available
0915 – 0930	Introductory remarks, announcements
0930 – 1030	Reports from other meetings/projects/countries – who else is doing/planning what? - *Wade McGillis*
1030 – 1045	BREAK, Coffee available
1045 – 1145	Basic logistics discussion - *Burke Hales*
1145 – 1200	General discussion on morning topics
1200 – 1330	LUNCH – provided for invited participants
1330 – 1430	Geochemistry and biogeochemistry discussion – *Rik Wanninkhof*
1430 – 1600	"Action Workshops" – Small groups collaborate, search literature, run calculations, determine missing data, etc.
1600 – 1630	BREAK – Coffee, Snacks
1630 – 1700	Reports on "Workshops" to full group; Organize transportation logistics for dinner
1700 – 1900	BREAK – travel to Piermont.
1900 – ~2200	Group Dinner for invited participants - Sidewalk Bistro, 482 Piermont Ave, Piermont, NY



LAMONT-DOHERTY EARTH OBSERVATORY
THE EARTH INSTITUTE AT COLUMBIA UNIVERSITY

Tuesday, 24 March 2009

0845 – 0915	Arrival at LDEO, Coffee available
0915 – 0930	Update remarks, announcements
0930 – 1030	BIOLOGY I: CO_2 effects on primary producers: Phytoplankton physiology, productivity, biomass, inorganic ballast production, assemblage changes – *Zackary Johnson*
1030 – 1045	BREAK, Coffee available
1045 – 1145	BIOLOGY II: CO_2 effects on fate of primary production: Heterotrophic cycling, microbial production, grazing, export – *Andy Juhl*
1145 – 1200	General discussion on morning topics
1200 – 1330	LUNCH – provided for invited participants
1330 – 1430	Modeling Discussion – *Mick Follows*
1430 – 1600	"Action Workshops" – Small groups collaborate, check literature, run preliminary calculations, determine missing data, etc.
1600 – 1630	BREAK – Coffee, Snacks
1630 – 1800	Reports on "Workshops" to full group Recap; progress made; yet to be done Determine format and authors of a product(s) documenting workshop outcomes and potential proposal ideas arising from this meeting
1800 – ~2000	Closing reception and buffet dinner – LDEO Comer Café Area.

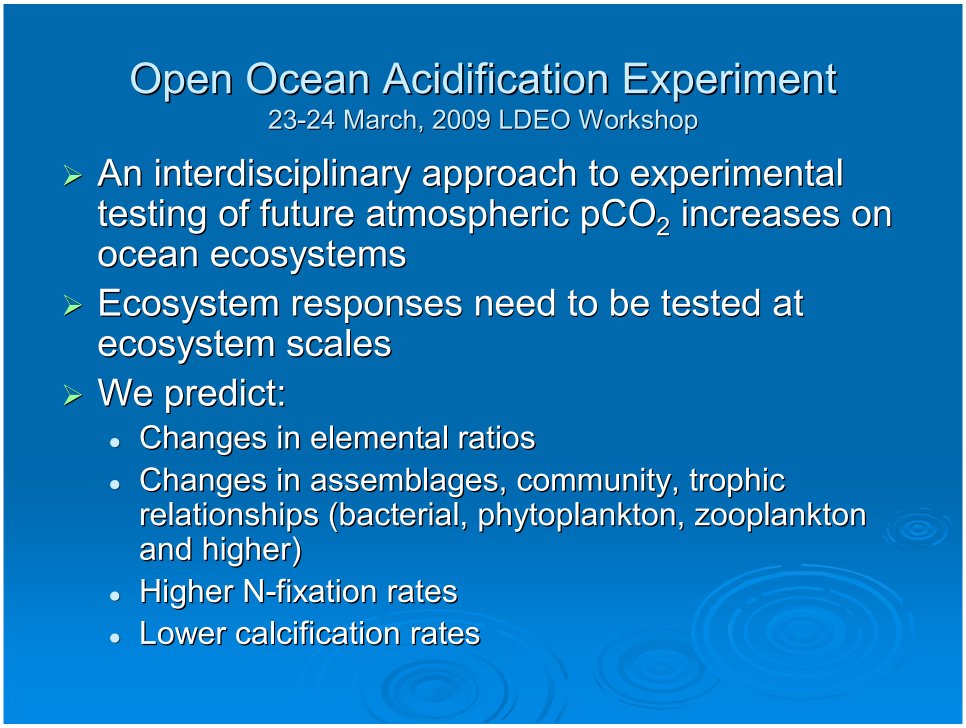
Many thanks to meeting sponsors:

LDEO Climate Center
LDEO Advisory Board Innovation Fund
NSF - ADVANCE at the Earth Institute of Columbia University

Appendix II
Meeting participants and attendees

Bob Anderson (LDEO)
O. Roger Anderson (LDEO)
Mick Follows (MIT)
Burke Hales (OSU)
David Ho (UH – SOEST)
Bärbel Hönisch (LDEO)
Zackary Johnson (Duke)
Andy Juhl (LDEO)
Adam Kustka (Rutgers)
Veronica Lance (LDEO)
Wade McGillis (LDEO)
Ray Sambrotto (LDEO)
Kris Swensen (LDEO)
Taro Takahashi (LDEO)
Rik Wanninkhof (NOAA – AOML)
Chris Zappa (LDEO)

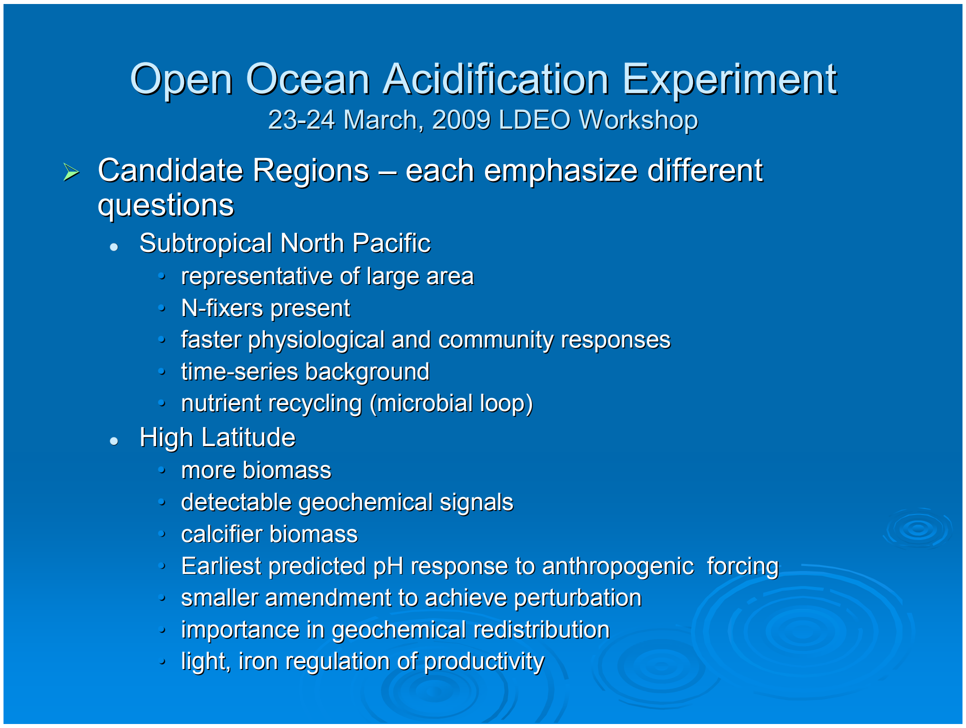
Appendix II
3 Slides for Wade McGillis presentation to International SOLAS meeting, 25-27 March 2009.



Open Ocean Acidification Experiment

23-24 March, 2009 LDEO Workshop

- An interdisciplinary approach to experimental testing of future atmospheric pCO_2 increases on ocean ecosystems
- Ecosystem responses need to be tested at ecosystem scales
- We predict:
  - Changes in elemental ratios
  - Changes in assemblages, community, trophic relationships (bacterial, phytoplankton, zooplankton and higher)
  - Higher N-fixation rates
  - Lower calcification rates



Open Ocean Acidification Experiment

23-24 March, 2009 LDEO Workshop

- Candidate Regions – each emphasize different questions
  - Subtropical North Pacific
    - representative of large area
    - N-fixers present
    - faster physiological and community responses
    - time-series background
    - nutrient recycling (microbial loop)
  - High Latitude
    - more biomass
    - detectable geochemical signals
    - calcifier biomass
    - Earliest predicted pH response to anthropogenic forcing
    - smaller amendment to achieve perturbation
    - importance in geochemical redistribution
    - light, iron regulation of productivity

Open Ocean Acidification Experiment

23-24 March, 2009 LDEO Workshop

- Vision of open ocean mari-corrals:
  - Semi-enclosed (open bottom and surface) marine corrals, multiple, large diameter (circa 100m)
  - Acidification addition (Δ 0.2 pH change; Δ ~200 μatm pCO_2)
  - Time scale ~weeks
  - Design, engineering and deployment utilizing commercial partners (commercial fisheries expertise)