Autonomous Observations of the Ocean Biological Carbon Pump

<PLATE 1> Carbon Flux Explorer at Dawn w R/V Sproul in the San Clemente Basin.

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Abstract

Prediction of the substantial biologically mediated carbon flows in a rapidly changing and acidifying ocean requires model simulations informed by observations of key carbon cycle processes on the appropriate space and time scales. From 2000 to 2004, the National Oceanographic Partnership Program (NOPP) supported the development of the first low-cost fully-autonomous ocean profiling Carbon Explorers that demonstrated that year-round real-time observations of particulate organic carbon (POC) concentration and sedimentation could be achieved in the world's ocean. NOPP also initiated the development of a sensor for particulate inorganic carbon (PIC) suitable for operational deployment across all oceanographic platforms. As a result, PIC profile characterization that once required shipboard sample collection and shipboard or shore based laboratory analysis, is now possible to full ocean depth in real time using a 0.2W sensor operating at 24 Hz. NOPP developments further spawned US DOE support to develop the Carbon Flux Explorer, a free-vehicle capable of following hourly variations of particulate inorganic and organic carbon sedimentation from near surface to kilometer depths for seasons to years and capable of relaying contemporaneous observations via satellite.

We have demonstrated the feasibility of real time - low cost carbon observations which are of fundamental value to carbon prediction and when further developed, will lead to a fully enhanced global carbon observatory capable of real time assessment of the ocean carbon sink, a needed constraint for assessment of carbon management policies on a global scale.

1. Introduction

The entire amount of marine phytoplankton biomass turns over on average once every 1 to 2 weeks, yet these short lived phytoplankton fix carbon at a rate of 40-50 Pg C y^{-1} and account for roughly half of global primary productivity (Antoine et al. 1996, Field et al., 1998, Falkowski et al., 1998, Westberry et al., 2008). Approximately 10 Pg C y^{-1} is exported below 100 m to the deep sea, mostly carried by sinking particles (Figure 1). This very fast process, commonly referred to as the ocean's "biological carbon pump" (Broecker and Peng, 1982; Volk and Hoffert, 1985), is important to the long term regulation of atmospheric CO_2 (Siegenthaler and Sarmiento, 1993) as it is one principal determinant of the vertical distribution of carbon in the ocean and hence of the surface partial pressure of CO_2 governing air-sea CO_2 exchange.

<Figure 1; Basic Carbon Cycle>

Figure 1 represents a steady state view of the carbon cycle with the down arrows of carbon export in balance with a net upwelling of water enriched with remineralized CO_2. The fact that the strength of the biological carbon pump has been estimated through a grand averaging of the decades of sparse ship observations of nutrient and carbon gradients in waters of the main pycnocline of the ocean means that it is not presently possible to determine from the observations if and how the biological carbon pump may be changing in response to rising atmospheric CO_2 levels through increasing ocean acidifcation and warming induced changes in stratification and circulation.

The effectiveness of the biological pump may be negatively impacted by the now readily detected ocean uptake of the anthropogenic CO_2 added to the atmosphere since the industrial revolution. The pH of today's surface ocean waters has decreased by ~0.1 units since the industrial revolution and is projected to decrease by another 0.3 units by 2100 (Sabine et al., 2004; Feeley et al. 2004). Current models predict that continued ocean acidification will lead to a decline in the productivity of calcium carbonate forming coral reef communities, calcifying shell fish, zooplankton (foraminifera and pteropods), phytoplankton (coccolithophores) in the coming decades (Orr et al. 2005; Kleypas et al., 2006; Fabry et al., 2008).

Towards better ocean carbon cycle predictions.

The only way to predict future trajectories of the global carbon cycle is through computer model simulations that accurately represent the substantial biotic carbon flows in the ocean. The parameterizations embedded within models for biotic carbon cycle processes are necessarily crude as they represent the sum of knowledge derived from observations which are sparse in time and space (Dickey et al., 2006; Buesseler et al., 2007a). A crucial parameter in these models is the carbon remineralization length scale, which summarizes how rapidly particulate organic carbon below the surface mixed layer (~100 meters thick) is converted to dissolved inorganic carbon (DIC) as the particles sink through the water column. A small remineralization length scale means rapid conversion, so that upwelling would bring high DIC to the surface and enhance outgassing of CO_2 to the atmosphere. Many ocean biogeochemistry models still use a single space- and time-invariant remineralization formula ($\Phi_Z = \Phi_{100}(Z/100)^{-b}$; b=0.86; Z is depth in meters; Φ_{100} is Sinking Carbon Flux at 100 m) derived from Martin et al.'s (1987) fair weather observations in the north Pacific, and cannot capture the roles of different biological regimes, or the impact of changes in ballast, among other things, on the global carbon cycle.

Already, limited ship observations provide compelling evidence that simple parameterizations of sedimentation are unrealistic. For example, Buesseler et al. (2007a) found very different remineralization length scales during summer time conditions in oliogotrophic waters near Hawaii (Martin b factor ~1.4) vs. productive waters of the Oyashio (b ~0.3) near Japan; Lam and Bishop (2007) showed that carbon remineralization length scales (independent of ballasting effects) were very different during summer conditions north and south of the Antarctic Polar Front (APF).

Some model parameterizations of carbon sedimentation and remineralization have evolved past the simple Martin formula but remain correlative and rely heavily on records from moored sediment traps deployed below 1000 m, much deeper than the typical remineralization depth (Armstrong et al. 2002; Dunne et al. 2005; Gehlen et al. 2006; Lutz et al. 2007), and extrapolations of sparse (and fair weather) near surface observations. Particulate organic carbon (POC) fluxes in the upper kilometer of the ocean are very under-observed and require great effort since all observations to date have required ships to be present (Buesseler et al., 2007b). Virtually no observations of the sedimentation of particulate inorganic carbon (PIC) have been made in the upper kilometer, yet the understanding of PIC dynamics is of fundamental importance to the biological carbon pump.

Calcium carbonate particles (predominantly coccoliths), when incorporated into organic matter rich aggregates are important contributors to excess density, i.e. the 'ballast', that causes these particles to sink (Armstrong et al., 2002). There is little known about how carbonate particle productivity will change and impact sedimentation. Riebesell et al., (2000) in laboratory cultures found a strong suppression of coccolithophore productivity with increasing CO_2. Iglesias-Rodriguez et al. (2008a) using a different laboratory methodology recently reported the opposite result. A decrease of the supply of carbonate ballast to aggregates could present an unexpected and amplifying

feedback as the remineralization of more slowly sinking aggregates would occur shallower in the water column and thus increase near-surface carbon concentrations and thus slowdown carbon uptake from the atmosphere. If the supply of ballast increases, higher particle sinking rates would lead to an enhanced biological carbon pump and increased CO_2 uptake. The sign of the change of coccolithophore productivity under increasing CO_2 is currently a debated point (Riebesell et al., 2008; Iglesias-Rodriguez et al 2008b). In other words, we don't know if the 10 Pg C y^{-1} bio-carbon pump (Figure 1) will be short-circuited or enhanced through changed carbonate ballasting. In-situ knowledge of carbonate dynamics would resolve these issues.

2. Carbon Explorers and Sensors

Autonomous technology, which promises to overcome the space-time gap in ocean bio-carbon observations, was first developed with National Oceanographic Partnership Program (NOPP) support (details are described in Section 4.0 below).

This article focuses on low-cost low-power carbon sensors and telemetry-enhanced ocean profiling Lagrangian floats and the use of these integrated systems to follow day-to-day variations of carbon biomass and flux. As will be shown below, Lagrangian platforms are ideally suited for carbon sedimentation measurements. The international program Argo [*CLIVAR*, 1999; Roemmich, this volume] has seeded the world's oceans with thousands of profiling Lagrangian floats to gather temperature and salinity profiles and information on mid-depth circulation for investigation of the climate state of the ocean. Argo floats are designed to profile to the surface from kilometer depths once every 10 days and record deep currents between profiles over 5 years. The Carbon Explorer, described next, was born from float technology developed for Argo but is designed to observe carbon processes on faster biological time scales needed for process understanding.

2.1 The Carbon Explorer

Since 2001, high-frequency (diurnal) exploration of particulate carbon dynamics in the upper 1000 m in the oceans has been possible using sensor-enhanced ocean profiling Argo-style floats, which are called Carbon Explorers (CE, Figure 2a). The profiling vehicle for the CE is a modified Sounding Oceanographic Lagrangian Observer (SOLO) float developed by NOPP partners at the Scripps Instrument Development Group (Russ Davis, Jeffrey Sherman, and Lloyd Regier). Explorers carried a transmissometer sensor, which yields a remarkably accurate estimate of POC concentration (Bishop et al., 2002; Bishop and Wood, 2008), and a light scattering sensor (Seapoint, Inc.) in addition to those for temperature and salinity. The transmissometer has also been used to determine the systematic fluctuations of sedimentation at depth (Bishop et al., 2004), which we call Carbon Flux Index (CFI, Figure 2b). CFI is the systematic measure of the rate of accumulation of particles on the upward looking transmissometer window during the time that the float is drifting at depth between profiles. The combination of in water physical parameters (T, S, and density) and particle sensitive optics, and satellite remotely sensed properties (winds, clouds, color) provide a powerful framework for understanding bio-carbon dynamics in the ocean.

<FIGURE 2 Carbon Explorer and Part of SOFeX POC and CFI record here>

Carbon Explorer Science. Carbon Explorers, yo-yoing up and down in the upper kilometer of the water column every day, have revealed exciting new insights into the biological pump. Biological productivity in the oceans requires not only light and macronutrients (e.g. NO_3, PO_4) but also micronutrients such as iron. The three great regions of oceans (Southern Ocean, Equatorial Pacific, and subarctic North Pacific) with high macronutrients and low productivity (HNLC) are assumed to be lacking in micronutrients. Mineral aerosols (dust), lofted from arid regions and transported long

distances in the atmosphere before deposition to the surface, are hypothesized to be a major source of iron to the oceans. With the first deployment of two Carbon Explorers in the North Pacific in April 2001, we (Bishop et al. 2002) documented for the first time the direct enhancement of marine productivity after an Asian dust storm, but found that episodes of dust-iron-enhanced marine productivity lasted only two weeks, much shorter than commonly believed. Prior to the CE, no ship expedition in the world's oceans had captured a time series of the biological response to dust deposition. Dust storms crossing over the north Pacific occur on average once every three years and it turned out that the April 2001 Gobi desert dust event that we observed was one of the biggest dust storms crossing the north Pacific in decades. Simply stated, by 'being there' for an entire year we had a one in three chance of observing a dust storm.

In 2002, the Carbon Explorers followed an iron 'fertilization' experiment in the HNLC Southern Ocean for 2 months from the beginning to the end of experiment and continued monitoring for another year after the ships had departed. CE's recorded the strong biological / carbon sedimentation response to purposeful iron amendment of low silicate – high nitrate waters near 55°S, 172°W during the Southern Ocean Iron Experiment (SOFeX; Coale et al., 2004). Two Explorers -- one deployed in iron amended waters and one deployed nearby as control -- completed 180 profiles each to depths of as great as 1000 m, three times per day until the effects of SOFeX iron were no-longer seen while at the same time they drifted for hundreds of kilometers in the Antarctic Circumpolar current. The finding of enhanced carbon export north of the Antarctic polar front in low silica high-nitrate waters was unexpected and invalidated the central hypothesis of SOFeX that iron amendment of low-silica waters would lead to a null result (Bishop et al. 2004).

The SOFeX Explorers continued operation in the stormy Southern Ocean following natural carbon cycle processes for another year (Bishop and Wood, 2009). One Explorer,

deployed at 66°S, 172°W, operated through the Antarctic winter in the ice edge zone, in 24 hour darkness, and returned an uninterrupted data stream to shore.

Track Record. Overall, the twelve CEs deployed to date have proved to be operationally robust (only one ended its mission prematurely and a thirteenth CE was lost on deployment after colliding with the ship). The record has demonstrated the utility of faster and bidirectional ORBCOMM telemetry: mission parameters could be changed post deployment and enough power was saved to permit the additional optical sensors and increases in profiling cycles. CE's typically achieved ~350,000 m of round trip profiling distance per float. Also demonstrated was that the optical sensors remained usable throughout their mission and suffered minimal biofouling effects and, with a single exception, all outlived the float.

Work is required to transition Carbon Explorers from ORBCOMM to Iridium telemetry to address data gaps for Explorers deployed in waters polewards of 50°N and S. CEs have been proven for both long-term monitoring and process studies.

2.2 Sensor for Particulate Inorganic Carbon (PIC)

As mentioned above, CO_2 acidification of the ocean is expected to impact calcifying plankton, and may impact carbon sedimentation in unexpected ways. There are fewer than several dozen published profiles of particulate inorganic carbon (PIC) in the world oceans based on shore-based laboratory analysis of filtered sea water samples; a shipboard method for PIC used optical back scattering measurements before and after acidification of ship collected water samples (Balch et al., 2002). There was a need for an autonomous chemistry-free sensor.

The PIC sensor (Figure 3A) developed with NOPP partner WETLabs, Inc., is designed permit rapid profiling of the ocean water column. It detects photons that interact with the strongly birefringent calcite and aragonite mineral forms of calcium carbonate.

Mineral particles in the ocean are by far dominated by calcium carbonate particles, which have an oceanic concentration range of 0.005 to 40 µM (Guay and Bishop, 2002).

In a modification of a 25 cm pathlength WETLabs Inc. C-Star transmissometer, light from a light emitting diode laser source is filtered such that it is polarized in the horizontal plane while at the same time the detector on the other end of a 25 cm open water path is guarded by a second high efficiency polarizer oriented to select only for vertically polarized light. In this way, the primary beam of light from the laser is blocked from passing to the detector. Suspended calcium carbonate minerals in the optical path partially depolarize the primary beam and thus give rise to a signal at the detector.

<FIGURE 3, (a) PIC sensor; (b) PIC profile at A16N (2003); (c) San Clemente Basin (2007)>

The first operational prototype ocean profiling PIC sensor (Figure 3a) was deployed during the 2003 CLIVAR repeat hydrography transect, A16N, in the North Atlantic. It rode the CLIVAR CTD rosette surface to the ocean floor hundreds of times. In the Iceland Basin waters where PIC levels were as high as several µM, its data replicated shipboard birefringence analyses (Guay and Bishop, 2002) of rosette collected water samples and replicated PIC distributions determined from chemical analysis of particulates filtered from parallel water samples. This first profiling sensor; however, had major thermal and pressure hysteresis effects and was not sufficiently stable for use in oligotrophic waters and much of the deep water where PIC levels are low. The PIC sensor was subsequently re-engineered and redeployed multiple times: from pole to equator, surface to bottom during the 2005 CLIVAR transect A16S in the South Atlantic; in the Oyashio (2005), San Clemente Basin (2007), and near Bermuda and in the Atlantic Slope Water (2008). The current fourth generation of this sensor is capable of 5-10 nM precision in the deep ocean (Figure 3c).

Two neutrally buoyant PIC sensors for the CE were also developed in 2003. One deployed on a CE in the Atlantic suffered a mechanical failure of its polarizing cell mounts but remained operating for the year long mission of the float. The second sensor remains in hand.

One final round of engineering will render the PIC sensor fully ready for transfer to the commercial sector. What once required ship collected samples and labor-intensive ship- or shore-based analysis now can be achieved at 24 Hz using a 0.2 W profiling sensor.

2.3 Optical Sedimentation Recorder and the Carbon Flux Explorer

Observations of carbon sedimentation in the upper kilometer of the ocean remain dependent on ships and are necessarily of short duration. This zone, that some refer to as the "forbidden zone" for carbon flux observations, is where substantial biological consumption (remineralization) of sinking organic particles occurs. We summarize below the development of the Optical Sedimentation Recorder (OSR) and the integration of the OSR with a highly modified SOLO float to produce a first prototype Carbon Flux Explorer (CFE; Figure 4).

<FIGURE 4 Carbon Flux Explorer and Optical Sedimentaton Recorder>

The Carbon Flux Explorer is an instrumental approach to observing POC and PIC sedimentation that is a logical, but substantially more challenging, but high pay-off extension of the simpler Carbon Explorers (CE) described in Section 2.1 and of the PIC sensor concept described in Section 2.2. It melds the concept of a neutrally buoyant sediment trap (NBST, Buesseler et al., 2000, 2007a; Stanley et al. 2004) with the concept of a camera imaging of the particles as they are deposited in a sediment trap (Asper, 1986). The power of the NBST approach is that it appears to avoid the hydrodynamic biases suffered by traditional surface tethered arrays of sediment traps (e.g. Gardner,

2000; Buesseler et al, 2007b). The strength of our present approach is that it enables high frequency (hourly to diel) observation of the variations of particle sedimentation using modern digital cameras and electronics; the current CFE design goal is sustained high-frequency observation of sedimentation processes for seasons to years. Together with satellite communications, the CFE has the potential to provide carbon sedimentation data in real time and operate in an experimental context absent of ships.

The Carbon Flux Explorer is aimed at providing mechanistic insight into the carbon sedimentation as well as to provide quantification of carbon flux. The CFE, for example, is capable of exploring the biological mechanisms and processes giving rise to the short term pulsing of sedimentation seen in Carbon Flux Index (CFI) records (Fig. 2b).

The Optical Sedimentation Recorder (Figure 4b), like all sediment traps, intercepts sinking particles. In our case, a funnel is used to concentrate particles onto a horizontal (flat) optical window. Looking upwards from below at the particles is a digital camera operating in macro focus mode. A 15 μm spatial image resolution is achieved over the entire sample collection area. The camera is outfitted with a motor-rotated high-efficiency polarizer. A stabilized low-power white-light source with attached fixed polarizer is suspended in the funnel and provides downward illumination so that particles can be imaged by the camera under transmitted parallel polarized light and transmitted cross polarized light. As mentioned above, cross-polarized transmitted light is effective for detecting highly birefringent calcium carbonate particles (Section 2.2). An annular ring light surrounding the sample collection area is used to achieve dark field illumination. Since all lighting systems are stabilized, raw RGB pixel counts in images can be reduced in terms of absolute reflectance/optical density.

Camera parameters are selected to match specific illumination modes. Three sets of images are taken sequentially separated in time by tens of seconds. Data are stored in memory external to the camera. Image cycles are typically separated in time by 30

minutes. Periodically after a number of image cycles (usually several hours), particles are removed from the sample area (in the case of surface buoy tethered versions of the OSR the discharge is directed into sample bottles; in the case of the Carbon Flux Explorer, the particles are discharged into the environment). An image cycle immediately following each cleaning provides a reference for subsequent images.

Control of camera, image transfers and storage, lighting, cleaning, and sampling systems is achieved by a combination of microcontroller and single board computer (SBC). On board batteries are currently capable of providing power to drive the OSR for one to two months. The OSR system developed for the Carbon Flux Explorer further is able to respond to event signals from the profiling SOLO (dive pending, surfacing pending, at depth, abort) and provides simple reduced image data, image thumbnails and OSR engineering parameters for real time transmission to shore and ship. Figure 5 illustrates how the three OST imaging modes are used to separate and identify particle components and phases.

<Figure 5 showing 3 imaging modes for the OST; samples obtained in near surface waters of the San Clemente Basin in 2007; 5b temporal variations of sedimentation Oyashio>

The ability of the CFE to operate in a temporal domain here-to-fore unobserved, yet able to sustain observations for months (current prototype) to seasons to years gives promise of a leap in observational carbon cycle oceanography using autonomous low powered platforms.

The CFE is currently an advanced engineering prototype and passed its first 3 day sea trial in mid 2007 (Figure 4). OSR instruments have operated for 40 days underwater and their sub-systems are stable. We need to learn if biofouling effects are minor (as they are for optical sensors on the Carbon Explorers) and if they are not, how to control them. We further need to learn about other long term operational characteristics of the CFE by

challenging it to progressively longer deployments in increasingly challenging ocean environments. It is one to two years from transfer to the commercial sector and the oceanographic community.

3.0 Summary and Prospects

Society needs prediction of the ocean carbon cycle, particularly of changes to the strength of the biological carbon pump. However, the understanding of the coupling between short lived surface processes and carbon sedimentation is hugely limited by a lack of observations.

Particulate carbon pools are small and turn over rapidly compared to dissolved inorganic and organic carbon pools and thus diurnal to seasonal variations of particulate carbon concentration and flux are readily observed to kilometer depths. For this reason we have focused on sensors for particulate organic and inorganic carbon pools and fluxes and on their integration with low-power long-lived Lagrangian floats. We have demonstrated two sensor approaches for Argo-style floats: (1) relatively small neutrally buoyant sensors which draw power from and are read by the electonics of the float, and (2) a fairly large and entirely autonomous and separate neutrally buoyant instrument package which listens to and communicates with the float when requested. Because our sensors have been developed for low power platforms, they can operate across all oceanographic platforms from ship-lowered CTD's to moorings, to high powered Autonomous Underwater Vehicles, and finally to Carbon Explorer cousins: buoyancy driven Gliders.

A Carbon Argo? The prospects are excellent for observation of the complete suite of carbon components from autonomous platforms over the next five to ten years. Ensemble deployment of Carbon Explorers (possible now) and Carbon Flux Explorers (possible in 1-2 years) in biologically dynamic oceans would lead to a quantum gain in understanding

of POC and PIC concentration and sedimentation variability, and thus lead to better parameterization of bio-carbon processes in model simulations. Such in-water systems will be invaluable for validation of satellite products such as those for PIC (e.g. Balch et al., 2005). Wider deployments of Carbon Explorers and Carbon Flux Explorers within an Argo style array would permit real time quantification and understanding of ocean carbon export.

On the horizon are sensors for other carbon components. Dissolved inorganic carbon pools exceed particulate pools by greater than three-orders-of-magnitude, and consequently sensors for detecting changes in dissolved inorganic carbon components must be parts per-thousand accurate or better in order to be useful (Millero, 2007). This is a significant challenge that is beginning to be met. For example, submersible sensors for the fugacity of CO_2 (fCO_2) have been deployed from moorings (DeGrandpre et al., 2006). These sensors currently have response times of ~5 minutes (vs. optical particle sensor response of fractions of a second) and need to be shorter for efficient profiling of the fCO_2 gradients in the water column. Dissolved organic carbon (DOC) comprises the dominant (>90%) fraction of the organic carbon pool in the ocean, and currently can only be determined by laboratory or shipboard analysis of water samples (Hansell et al., 2002). Preliminary experiments at LBNL suggest that low-power sensors for major components of the dissolved organic carbon pool (DOC) are feasible.

Russ Davis (personal communication) has pointed out that float profiling speeds (currently ~ 10 m/minute) may be controlled in near surface waters to match the response times of the current generation of slow CO_2 system sensors. At the same time, he says that it is important to recall that Argo floats were developed with the Argo mission in mind ten to fifteen years ago. Investment in float and sensor engineering to meet the needs of a C-Argo mission is a logical expectation. In other words, floats built for the Argo mission are not optimized for biogeochemical sensors.

While there is great focus on "wedge" strategies (conservation, nuclear, carbon sequestration, … c.f. Pacala and Socolow, 2004) to offset or reduce CO_2 emissions (now at 8 Pg C y^{-1}) to the atmosphere, an integrated carbon management strategy must include monitoring and prediction of the 10 Pg C y^{-1} biological carbon pump. With a suite of fully integrated carbon sensors, it would be possible to determine the net carbon transfers from atmosphere to surface ocean, its distribution among time varying carbon pools, and transfer efficiency to deep sea in real time. With the right investment, and partnering between educational, governmental, and commercial sectors, a Carbon Argo (C-Argo) program, combining multiple autonomous platform types and carbon sensors, could yield real time assessment of global ocean carbon fluxes at a time when such data are desperately needed.

4.0 History of this partnership.

I was first captivated by the possibilities of autonomous ocean carbon observations by a World Ocean Circulation Experiment (WOCE) study that took place in the mid 1990's when 200 autonomous profiling floats were deployed in the Labrador Sea (Lavender, Davis and Owens, 2000) to observe the formation and transport of Labrador Sea Water (LSW). I recall attending the Labrador Sea session at the 1998 AGU Ocean Sciences Meeting and learning how the understanding of the formation and dynamics of LSW had just become "overturned" by this quantum jump in observational capability and saying to myself, "Imagine what we could learn if we could do this kind of experiment for the carbon cycle". I rushed over to Russ Davis to broach the idea of carbon observations on floats and the nucleation of our NOPP project was begun. The Scripps Instrument Development Group was beginning work on the Spray Glider. Since this self-navigating autonomous vehicle required bi-directional satellite telemetry and IDG was investigating the ORBCOMM system, testing it using IDG's Sounding Oceanographic Lagrangian Observer (SOLO), would speed the development of Spray and exercise SOLO is a way

that would increase its reliability for the upcoming Argo program. ORBCOMM telemetry would reduce the time at surface for data transmission from days to tens of minutes and thus enable deployment of optical sensors by minimizing exposure to biofouling conditions. WETLabs, Inc. would work to stabilize transmissiometer electronics and provide their transmissometer in a neutrally buoyant package capable of 2000 m. WETLabs would further provide several embodiments of a new sensor for particulate inorganic carbon. A successful proposal (leveraged with DOE projects and a NOAA postdoctoral fellowship grant) to the NOPP 1999 competition, led to perhaps one of the most enjoyable projects of my career.

The partnership of LBNL, Scripps (Instrument Development Group), and WETLabs, Inc. led to the eventual deployment of 12 Explorers world wide under the original NOPP (3), and new NOAA (5) and DOE (4) supported projects. This NOPP partnership was recognized by receiving the 2006 R&D 100 Award for developing the Carbon Explorer. WETLabs, Inc. has marketed the neutrally buoyant C-Rover transmissometer for floats, which was a direct outgrowth of our NOPP effort. US Patent #7,030,981 was awarded in 2006 to the Lawrence Berkeley National Laboratory for the PIC sensor concept.

Acknowledgements.

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Bishop (Oceanography article figure captions)

Plate 1. Carbon Flux Explorer awaiting recovery at dawn at the end of its first 1.5 day mission in the San Clemente Basin near San Doego, June 2007. R/V Sproul is in the background.

Figure 1. Steady state representation of the carbon pools (Pg C – in italics) and transports (Pg C y^{-1} in parentheses) for mid 1990's representing the synthesis of decades of ship observations. Diagram based on recent summary views of the large scale carbon cycle (Denman et al., 2007; Sarmiento and Gruber, 2006) with updates on particulate inorganic carbon fluxes and stocks (Berelson et al., 2006; author's unpublished data), and the author's extrapolation of Hansell et al. (2002) data on dissolved organic carbon transports due to intermediate water formation. The biological carbon pump (leading to carbon sedimentation) is very fast, and dynamic and poorly observed in space and time. The central unanswered question is whether or not carbon sedimentation is changing in a rapidly changing world. What changes are in store for the future? Our focus is on development of autonomous sensors for particulate organic carbon (POC) and particulate inorganic carbon (PIC) concentration and flux.

Figure 2. Top. Carbon Explorer showing optical transmissometer (A) and scattering (B) sensors. The transmissometer has been configured to permit the determination of the systematic variations of carbon sedimentation. While the float is at depth between profiles, particles accumulate on the upward looking window of the transmissometer (C). Prior to profile operations, the transmissometer is read, the window flushed clean with flowing seawater, and the transmission reading determined a second time. The difference in transmission normalized by time at depth between profiles is the Carbon Flux

Index (CFI). (Bottom) POC concentration time series from the Antarctic Circumpolar Current near 55°S 170°W (from Bishop et al., 2004). Shown in red is the systematic variation of Carbon Flux Index (CFI) at 100 m.

Figure 3. (a) Sensor for particulate inorganic carbon (PIC) capable of full water column profiles based on a WETLabs 25 cm C-Star transmissometer. (1) LED laser light source, (2) a first in-line polarizer filters laser light into the horizontal plane, (3) the second 'guard' polarizer over detector window is oriented to pass only vertical plane polarized light, (4) detector. Birefringent calcium carbonate particles in the open 25 cm water path depolarize the primary beam and thus lead to photons passing the guard polarizer to the detector. (b) PIC sensor profile from the Iceland Basin in 2003 (A16N Station 8). Circles – shipboard birefringence analysis of filtered water samples. Triangles – PIC concentrations determined by inductively coupled plasma mass-spectrometry (ICP-MS) in particulates filtered from rosette collected water samples. The sensor in 2003 was had a precision of only ~0.1 to 0.2 μM PIC. It has been since modified multiple times. (c) Down and up cast profiles from the 4th generation PIC sensor and ICP-MS determined PIC from water samples obtained during a 2007 CTD-rosette cast in the San Clemente Basin. The agreement of up and down casts is of the order of 0.005 μM in deep water. The PIC sensor is capable of detection of PIC over the entire oceanic range (~0.005 μM to 40 μM). Minor work remains to commercialize this sensor.

Figure 4. (a) Schemeatic of the Carbon Flux Explorer. The CFE represents the integration of the Optical Sedimentation Recorder (OSR; engineered at Berkeley Lab) and the Sounding Oceanographic Lagrangian Observer (SOLO; Scripps) profiling float. (b) Optical Sedimentation Recorder (OSR), an instrument designed to quantify carbon sedimentation on hourly time scales for seasons.
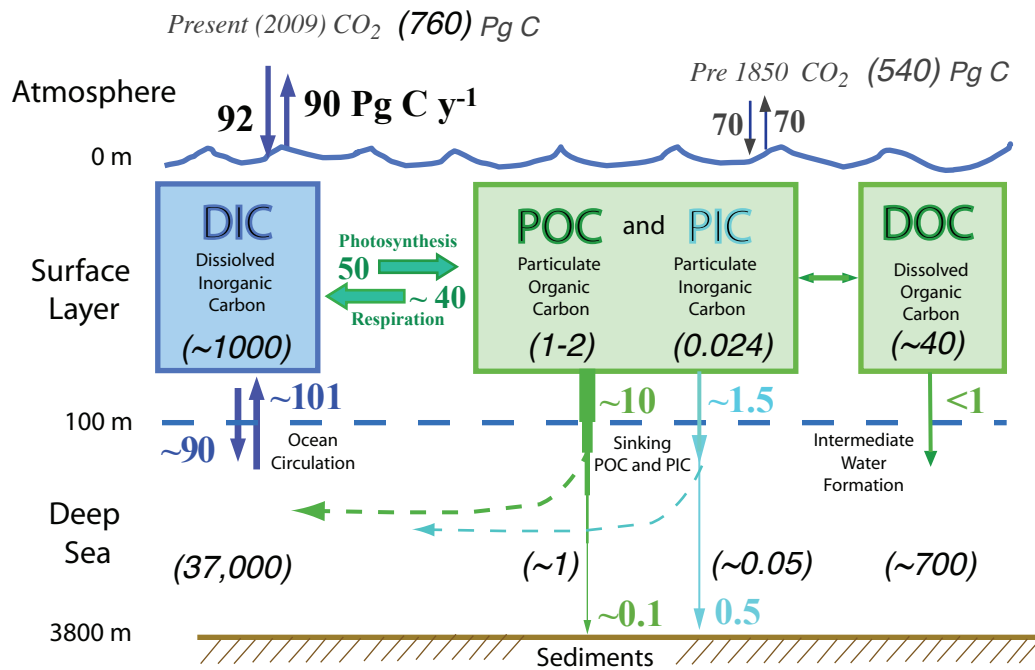
The SOLO communicates to the OSR it's dive status and pending actions. The OSR communicates reduced data to the SOLO for relay to Iridium satellites.
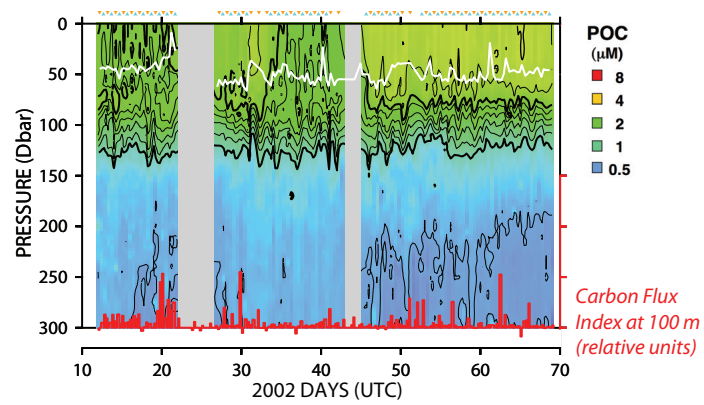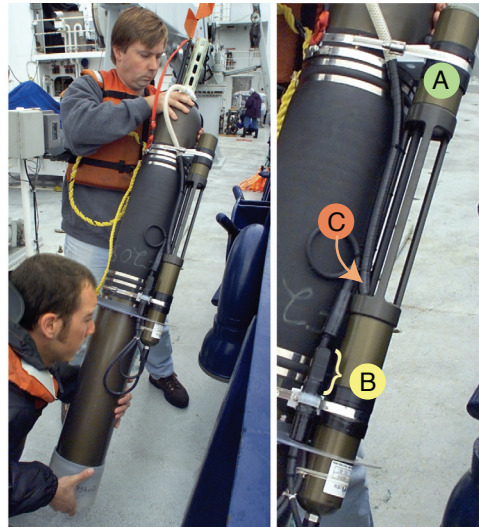
Figure 5. (a) Images of particles from the Carbon Flux Explorer deployment in 2007 San Clemente Basin, near San Diego, CA. The three modes of imaging, Dark Field (side illuminated), Transmitted, and Cross Polarized (Cross Polarized Transmitted light) allow identification and separation of major particle phases from the upper water column ~50 m. Right: Carbonates (small Foraminifera) indicated by blue lines are readily seen as bright spots in cross polarized images; The bright haze in the aggregate and in part of the fecal pellet is due to micron-sized calcium carbonate coccoliths. Green circle contrasts images of a fecal pellet. Note, either the carbonate has dissolved in part of the fecal pellet at the left of all images or that the grazer had changed its diet. (b) Raw dark field RGB image counts integrated over the OST sample collection area show particle accumulation in successive image cycles. Cleaning cycles (1,7,14,21...) occurred once every ~2.5 hours, images were taken at 25 minute intervals. A rarely photographed organism is present during cycle 39 in the 5th set of images - data from cycles 39-41 are excluded based on movement of particles and the sudden drop of integrated count after the organism departed. (c) Flux variability by first difference of CCD counts. Maximum sedimentation flux occurred at 0200 local time. Sedimentation varied by a factor of ten on an hour to hour basis.

Figure Spread For Article (Available at full 40 MB - professional Resolution)

Carbon Flux Explorer at dawn June 22 2007 San Clemente Basin after 1.5 day operation to 800 m. R/V Sproul is in the background. Photo by Roy Kaltschmidt, LBNL.

Present (2009) CO$_2$ **(760)** *Pg C*

Atmosphere

Pre 1850 CO$_2$ **(540)** *Pg C*

92 | **90 Pg C y^{-1}**

70 | **70**

0 m

DIC
Dissiolved
Inorganic
Carbon

(~1000)

Photosynthesis
50
~ 40
Respiration

POC and PIC
Particulate
Organic
Carbon

Particulate
Inorganic
Carbon

(1-2)   *(0.024)*

DOC
Dissolved
Organic
Carbon

(~40)

Surface
Layer

~101

~10   **~1.5**

<1

100 m

~90

Ocean
Circulation

Sinking
POC and PIC

Intermediate
Water
Formation

Deep
Sea

(37,000)

(~1)

(~0.05)

(~700)

3800 m

~0.1   **0.5**

Sediments

POC
(μM)
■ 8
■ 4
■ 2
■ 1
■ 0.5

Carbon Flux
Index at 100 m
(relative units)

(a)

(b)

Particulate Inorganic Carbon (µM)

Ron Brown 2003
Iceland Basin
A16N station 8

⊙ Shipboard (10 min/sample)
△ ICP-MS PIC

T

(c)

Particulate Inorganic Carbon (µM)

R/V Sproul 2007
San Clemente Basin

dots (down cast)
solid line (up cast)
△ ICP-MS PIC

T

(a)   *(b)*

Argos

Iridium

light

funnel

imaging
stage

imager

cpu &
controller

batteries

(a)

1 mm

Dark Field   Transmitted   Cross Polarized Transmitted

POC containing aggregates

PIC in Foraminifera shells

PIC in coccoliths and Foraminifera shells in aggregates

(b)

Optical Sedimentation Recorder
150 m Oyashio

green
blue
red

Raw RGB counts x 10⁶

Cleaning

organism detected

Image Cycle

(c)

18   00   06   12   18
night   day
record

Green counts/hour x 10⁶

organism

Cleaning

Hours (UTC)