Autonomous Observations of the Ocean Biological Carbon Pump

BY JAMES K.B. BISHOP

Carbon Flux Explorer awaiting recovery at dawn at the end of its first 1.5-day mission in the San Clemente Basin near San Diego, CA, June 2007. R/V *Sproul* is in the background. *Photo credit: Roy Kaltschmidt, Lawrence Berkeley National Laboratory*

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 spatial and temporal 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, which 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 particulate inorganic carbon (PIC) sensor 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 0.2-W sensor operating at 24 Hz. NOPP developments further spawned US Department of Energy support to develop the Carbon Flux Explorer, a free vehicle capable of following hourly variations of PIC and POC sedimentation from the 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 that are of fundamental value to carbon prediction and that, 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.

INTRODUCTION

The entire amount of marine phytoplankton biomass turns over, on average, once every one to two weeks, yet these short-lived phytoplankton fix carbon at a rate of 40–50 petagrams (Pg) C y^{-1} and account for roughly half of global primary productivity (Antoine et al., 1996; Falkowski et al., 1998; Field 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 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 decades of sparse ship observations of nutrient and carbon gradients in waters of the ocean's main pycnocline 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 acidification 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 shellfish, zooplankton (foraminifera and pteropods), and phytoplankton (coccolithophores) in the coming decades (Orr et al., 2005; Kleypas et al., 2006; Fabry et al., 2008).

Toward 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 that 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 (POC) below the surface mixed layer (~100-m thick) is converted to dissolved inorganic carbon (DIC, the sum of CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-} species) as the particles sink through the water column. A small remineralization length scale means that conversion of sinking POC back to CO_2 occurs closer to the surface,
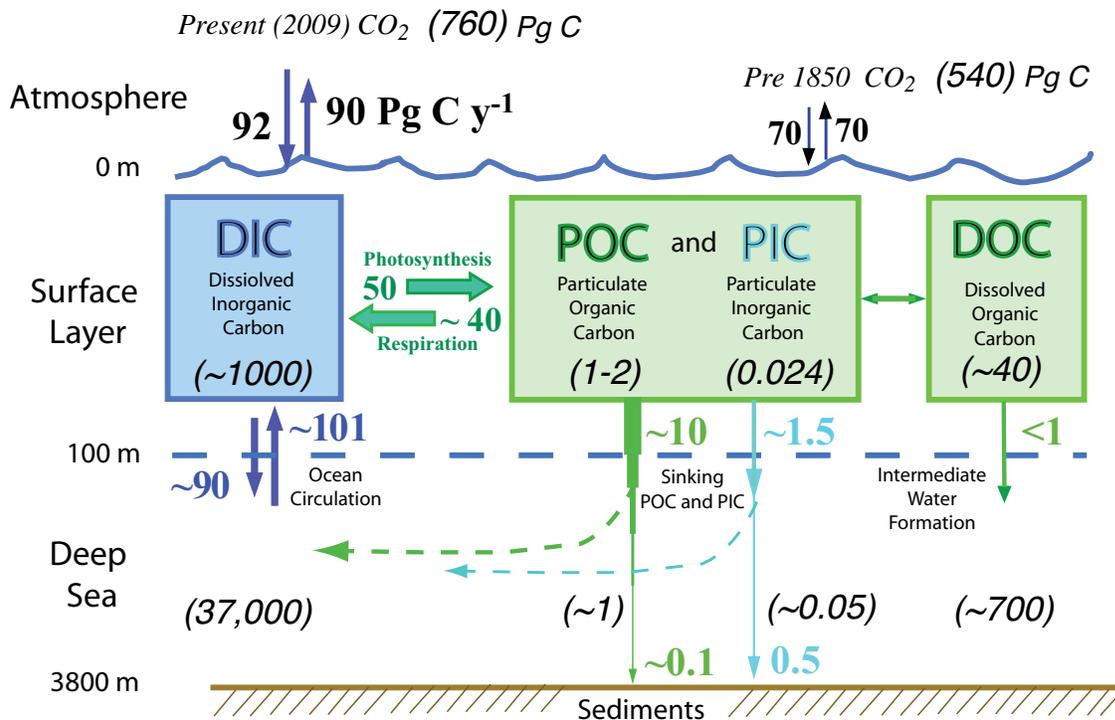
Present (2009) CO$_2$ **(760)** *Pg C*

Atmosphere

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

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

70 **70**

0 m

DIC
Dissolved
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

100 m

~**101**

~**10** ~**1.5** <**1**

~**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

Figure 1. Steady-state representation of the carbon pools (Pg C, in italics and parentheses) and transports (Pg C y^{-1}, next to arrows) for the mid 1990s representing the synthesis of decades of ship observations. The diagram is 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. PIC is composed of calcium carbonate minerals, calcite and aragonite. Light dashed lines denote remineralization of POC and PIC back to DIC. 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.

thus upwelling would bring water enriched in CO$_2$ back to the surface faster and thus decrease the capacity of the ocean to take up CO$_2$ from 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

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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 (or dense biogenic mineral particles such as calcium carbonate or opaline silica that give sinking aggregate particles negative buoyancy; Armstrong et al., 2002) 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 summertime conditions in oliogotrophic waters near Hawaii (Martin b factor ~ 1.4) vs. productive waters of the Oyashio Current (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.

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. POC fluxes in the upper kilometer of the ocean are very under-observed and require great effort because all observations to date have required ships to be present (Buesseler et al., 2007b). Virtually no observations of particulate inorganic carbon (PIC) sedimentation 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"), which causes these particles to sink (Armstrong et al., 2002). Little is known about how carbonate particle productivity will change and impact sedimentation. Riebesell et al. (2000), in laboratory cultures, found 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 in 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 slow down carbon uptake from the atmosphere. If the supply of ballast increases, higher particle sinking rates would lead to an enhanced biological carbon pump and

> "...UNDERSTANDING THE COUPLING BETWEEN SHORT-LIVED SURFACE PROCESSES AND CARBON SEDIMENTATION IS HUGELY LIMITED BY A LACK OF OBSERVATIONS."

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.

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 in the last section of this paper).

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 issue) has seeded the world's ocean with thousands of profiling Lagrangian floats to gather temperature and salinity profiles and information on mid-depth circulation for investigation of the ocean's climate state. Argo floats are designed to profile to the surface from kilometer depths once every 10 days and

record deep currents between profiles over five 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.

The Carbon Explorer

Since 2001, high-frequency (diurnal) exploration of particulate carbon dynamics in the upper 1000 m in the ocean has been possible using sensor-enhanced, ocean-profiling Argo-style floats, called Carbon Explorers (CEs, Figure 2a). The profiling vehicle for 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 carry a transmissometer sensor developed by NOPP partner WET Labs Inc., 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 sensors for temperature and salinity measurements. The transmissometer has also been used to determine systematic sedimentation fluctuations at depth (Bishop et al., 2004), which we call the Carbon Flux Index (CFI, Figure 2b). CFI is the systematic measure of the rate of particle accumulation on the upward-looking transmissometer window during the time that the float is
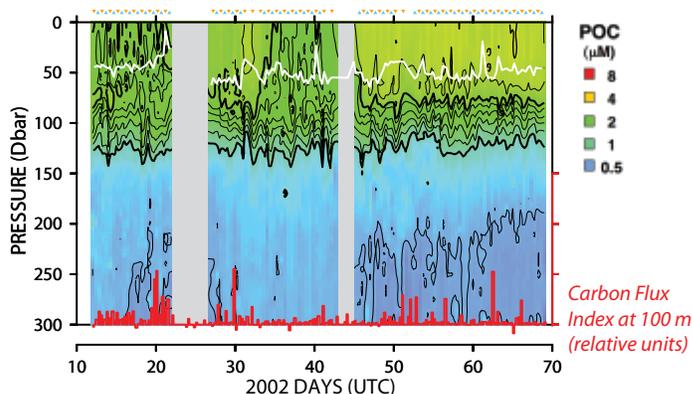
Figure 2. (Top) Carbon Explorer showing optical transmissometer (A) and scattering (B) sensors. The transmissometer has been configured to permit determination of the systematic variations of carbon sedimentation. While the float is at depth between profiles, particles accumulate on the upward-looking 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) Particulate organic carbon (POC) concentration time series from the Antarctic Circumpolar Current near 55°S, 170°W (from Bishop et al., 2004). The POC time series was constructed from dawn, mid-day, and dusk profiles from 1000, 300, and 300 m, respectively. Systematic variation of CFI measured at 100 m is shown in red.

micronutrients such as iron. The three great ocean regions (Southern Ocean, Equatorial Pacific, and subarctic North Pacific) exhibiting 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 ocean. With the first deployment of two Carbon Explorers in the North Pacific in April 2001, 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 Carbon Explorer, no ship expedition in the world's ocean 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, CEs followed an iron "fertilization" experiment in the HNLC Southern Ocean for two months, from the beginning to the end of the experiment, and continued monitoring for another year after the ships had departed. CEs recorded 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.,

drifting at depth between profiles. The combination of in-water physical parameters (T, S, density) and particle-sensitive optics, along with satellite remotely sensed properties (winds, clouds, color) provides a powerful framework for understanding bio-carbon dynamics in the ocean.

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 ocean requires not only light and macronutrients (e.g., NO_3, PO_4) but also

2004). Two Explorers—one deployed in iron-amended waters and one deployed nearby as control—while drifting for hundreds of kilometers in the Antarctic Circumpolar current, completed 180 profiles, each to depths as great as 1000 m, three times per day, until the effects of SOFeX iron were no longer seen. 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, in press). One CE, 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.

Overall, the 12 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 demonstrates the utility of faster and bidirectional ORBCOMM Inc. telemetry: mission parameters could be changed post deployment, and enough power was saved to permit the additional optical sensors and increases in profiling cycles. CEs typically achieved ~ 350,000 m of round-trip profiling distance per float. The optical sensors remained usable throughout the mission, suffered minimal biofouling effects, and, with a single exception, all outlived the floats.

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

Sensor for Particulate Inorganic Carbon

As mentioned above, CO_2 acidification of the ocean is expected to impact calcifying plankton, and may impact carbon sedimentation in unexpected ways. Fewer than several dozen PIC profiles of the world's ocean have been published on shore-based laboratory analysis of filtered seawater samples; a shipboard method for PIC used optical backscattering 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 WET Labs Inc. is designed to permit rapid profiling of the ocean's 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 WET Labs Inc. C-Star transmissometer, light from a light-emitting diode laser source is filtered such that it is polarized in the horizontal plane while 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.

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 conductivity-temperature-depth (CTD) rosette from the surface to the ocean floor hundreds of times. In Iceland Basin waters where PIC levels were as high as several µM, its data replicated shipboard birefringence analyses of rosette-collected water samples (Guay and Bishop, 2002) 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 and surface to bottom during the 2005 CLIVAR transect A16S in the South Atlantic and in the Oyashio Current (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 Explorer 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 float's year-long mission. The second sensor remains in hand.
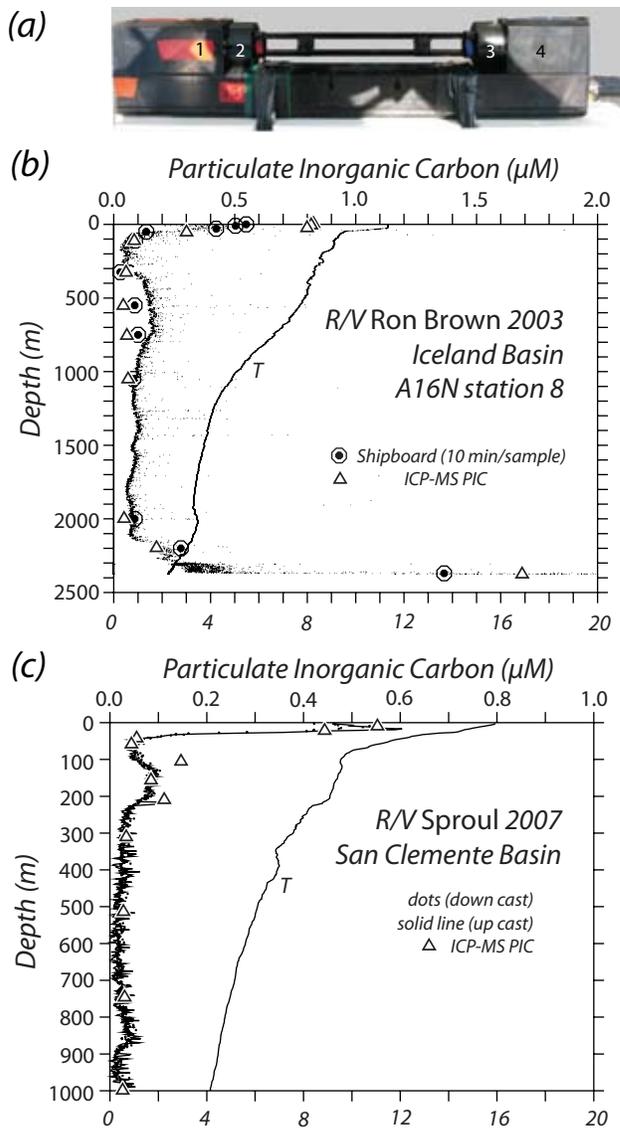
(a)

(b)

Particulate Inorganic Carbon (µM)

R/V Ron Brown *2003*
Iceland Basin
A16N station 8

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

T

Depth (m)

(c)

Particulate Inorganic Carbon (µM)

R/V Sproul *2007*
San Clemente Basin

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

T

Depth (m)

Figure 3. (a) Sensor for particulate inorganic carbon (PIC) capable of full water-column profiles based on a WET Labs Inc. 25 cm C-Star transmissometer. (1) LED laser light source. (2) First in-line polarizer, which filters laser light into the horizontal plane. (3) Second "guard" polarizer over the detector window, 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 indicate shipboard birefringence analysis of filtered water samples, and triangles indicate PIC concentrations determined by inductively coupled plasma mass-spectrometer (ICP-MS) analysis of particulates filtered from rosette-collected water samples. The sensor used in 2003, which had a precision of only ~ 0.1 to 0.2 µM PIC, has been modified multiple times since. (c) Down and up cast profiles from the fourth-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 detecting PIC over the entire oceanic range (~ 0.005 µM to 40 µM). Minor work remains to commercialize this sensor.

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.

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, which 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 OSR with a highly modified SOLO float to produce a first prototype Carbon Flux Explorer (CFE; Figure 4 and title page photo).

The instrumental CFE approach to observing POC and PIC sedimentation is a logical, but substantially more challenging, high pay-off extension of the simpler CE and PIC sensor concept described above. 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 that images 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 particle sedimentation

variations 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, CFE has the potential to provide carbon sedimentation data in real time and operate in an experimental context absent ships.

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

OSR (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. A digital camera operating in macro focus mode looks upward at the particles on the window. 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 a fixed polarizer attached 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. An annular ring light surrounding the sample collection area is used to achieve dark field illumination. Because all lighting systems are stabilized, raw RGB pixel counts in images can be reduced in terms of absolute reflectance/optical density.
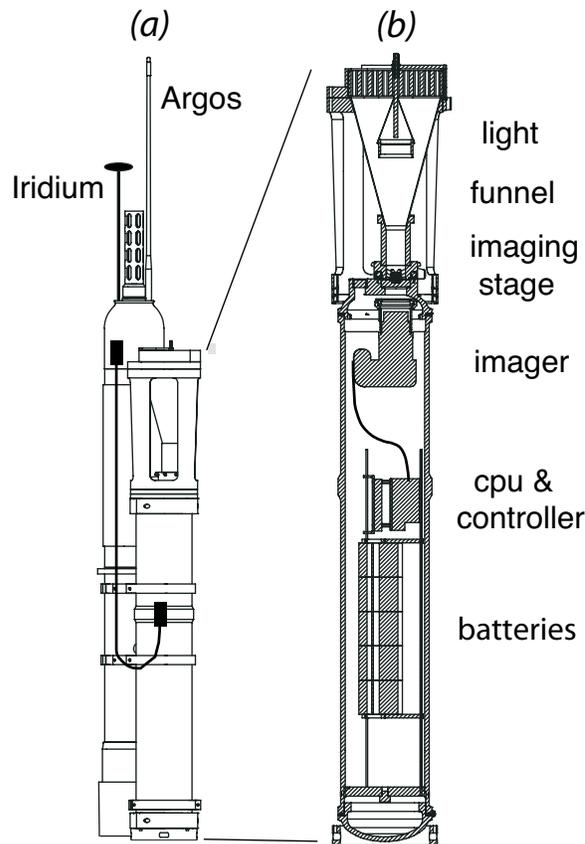

Figure 4. (a) Schematic of the Carbon Flux Explorer (CFE). CFE represents the integration of the Optical Sedimentation Recorder (OSR, engineered at Berkeley Lab) and the Sounding Oceanographic Lagrangian Observer (SOLO; Scripps) profiling float. (b) Optical Sedimentation Recorder (OSR). This instrument was designed to quantify carbon sedimentation on hourly time scales for seasons. SOLO communicates its dive status and pending actions to OSR and OSR communicates reduced data to SOLO for relay to Iridium satellites.

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 OSR, the discharge is directed into sample bottles; in the case of CFE, 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). Onboard batteries are currently capable of providing power to drive the OSR for one to two months. The OSR system developed for CFE is also 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 OSR imaging modes are used to separate and identify particle components and phases.

CFE's ability to operate in a temporal domain, heretofore 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.
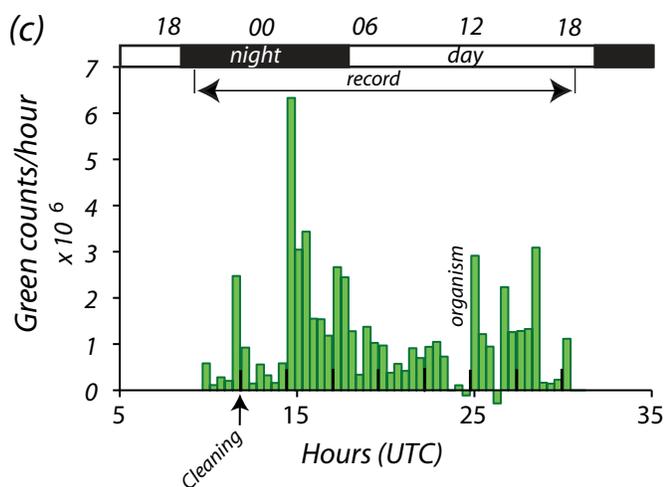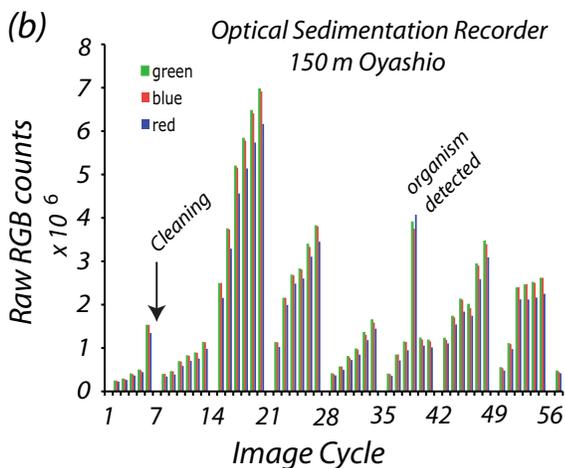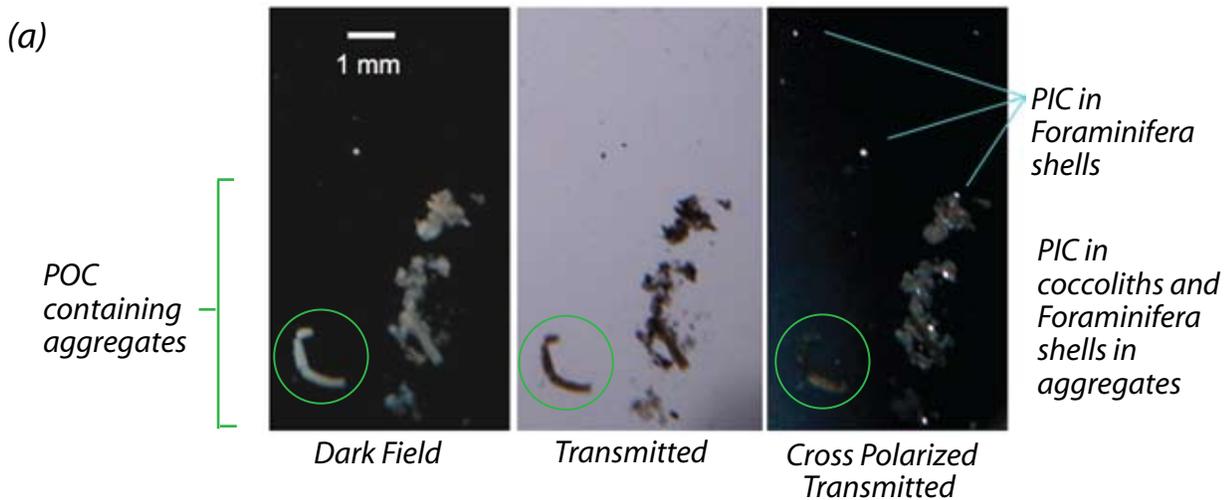
Figure 5. (a) Images of particles from the Carbon Flux Explorer deployment in 2007 in the San Clemente Basin, near San Diego, CA. The three modes of imaging, dark field (side illuminated), transmitted, and cross polarized (cross-polarized transmitted light) allow identification and separation of major particle phases. Shown is a "zoomed" area of one image set of particles collected at ~ 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. The green circle contrasts images of a fecal pellet. Note that either the carbonate has dissolved in part of the fecal pellet at the left of all images or the grazer had changed its diet. (b) Raw dark field RGB image counts integrated over the OSR 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 fifth 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 charge-coupled device counts. Maximum sedimentation flux occurred at 0200 local time. Sedimentation varied by a factor of ten on an hour-to-hour basis.

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

SUMMARY AND PROSPECTS

There is a societal need to predict the ocean carbon cycle, particularly changes to the strength of the biological carbon pump. However, understanding 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 focused on sensors for measuring POC and PIC pools and fluxes, and their integration with low-power, long-lived Lagrangian floats. We demonstrated two sensor approaches for Argo-style floats: (1) relatively small, neutrally buoyant sensors that draw power from and are read by the float's electronics, and (2) a fairly large and entirely autonomous and separate neutrally buoyant instrument package that listens to and communicates with the float when requested. Because our sensors were developed for low-power platforms, they can operate across all oceanographic platforms, from ship-lowered CTDs, to moorings, to high-powered AUVs, and finally, to CE cousins: buoyancy-driven gliders.

A Carbon Argo?

The prospects are excellent for observing the complete suite of carbon components from autonomous platforms over the next five to ten years. Ensemble deployment of CEs (possible now) and CFEs (possible in one to two years) in the biologically dynamic ocean 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 CEs and CFEs within an Argo-style array would permit real-time quantification and understanding of ocean carbon export.

Sensors for other carbon components are on the horizon. Dissolved inorganic carbon pools exceed particulate pools by greater than three orders of magnitude; consequently, sensors for detecting changes in dissolved inorganic carbon components must be parts-per-thousand accurate or better to be useful (Millero, 2007). This significant challenge is beginning to be met. For example, submersible sensors for CO_2 fugacity (fCO_2) have been deployed from moorings (DeGrandpre et al., 2006). These sensors currently have response times of about five minutes (as opposed to optical particle sensor response of fractions of a second), which are too long 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 Lawrence Berkeley National Laboratory suggest that low-power sensors for major components of the DOC pool are feasible.

Russ Davis (Scripps Institution of Oceanography, *pers. comm.*, December 2008) has pointed out that float profiling speeds (currently ~ 10 m min^{-1}) 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 10 to 15 years ago. Investment in float and sensor engineering to meet the needs of a Carbon Argo (C-Argo) mission is a logical expectation. In other words, floats built for the Argo mission are not optimized for biogeochemical sensors.

Although there is great focus on "wedge" strategies (e.g., 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 the atmosphere to the surface ocean, its distribution among time-varying carbon pools, and transfer efficiency to the deep sea in real time. With the right investment, and partnering among educational, governmental, and commercial sectors, a 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.

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 1990s when 200 autonomous profiling floats were deployed in the Labrador Sea (Lavender et al., 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 began. The Scripps Instrument Development Group (IDG) was beginning work on the Spray Glider. Because this self-navigating autonomous vehicle required bi-directional satellite telemetry and IDG was investigating the ORBCOMM system, testing it using IDG's SOLO would speed development of the Spray Glider and exercise SOLO in 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. WET Labs Inc. would work to stabilize transmissometer electronics and provide the company's transmissometer in a neutrally buoyant package capable of 2000 m. WET Labs 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 Lawrence Berkeley National Labs, Scripps Institution of Oceanography (IDG), and WET Labs Inc. led to the eventual deployment of 12 CEs worldwide under the original NOPP (3 CEs), and new NOAA (5) and DOE (4) supported projects. This NOPP partnership was recognized with the 2006 R&D 100 Award for developing the Carbon Explorer. WET Labs 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.

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