# Autonomous Profilers for Carbon System and Biological Observations

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## LONG-TERM GOALS

Our long-term goal is to understand the biogeochemical dynamics of the upper kilometer of the water column. Such an understanding is fundamental to the prediction of the processes partitioning carbon between atmosphere and ocean and to the redistribution of carbon and associated elements within the water column. Key to predictability is understanding day-to-day to seasonal variability of processes governing carbon species (dissolved and particulate, inorganic and organic) in the water column.

## OBJECTIVES

Our objective is to demonstrate the concept of low-cost autonomous profiling vehicles, outfitted with a suite of low-power optical, physical and chemical sensors. When widely deployed, these will permit high frequency four-dimensional observations of the variability of ocean biological processes, carbon biomass, upper ocean physics, and parameters of the carbon system in the upper 1000 m. It is envisioned that once proven, such vehicles can be widely deployed to explore carbon variability on global scales. An immediate objective is to demonstrate that we can explore carbon biomass variability in the water column on daily to seasonal time-scales in remote and extreme environments.

## APPROACH

*Platform*. The autonomous platform to be used is the Sounding Oceanographic Lagrangian Observer (SOLO; Davis et al., 2000), a low-cost autonomous profiling float. This well-proven ocean physics platform, augmented with new optical sensors for biogeochemistry, will permit the rapid and precise determination of two important products of photosynthesis, particulate organic carbon (POC) and particulate inorganic carbon (PIC), as well as physical data (T, S and derived density stratification) relevant to understanding the variability of these products. SOLO will be modified to accommodate POC and PIC sensors and with ORBCOMM transceivers for bi-directional telemetry of data at much higher data rates than the previously used System Argos.

Implementation of the faster telemetry permits transmission of data from the expanded sensor suite while significantly reducing the time (and hence susceptibility to biofouling) of the float in the surface layer. SIO leads the modification of SOLO. Coordination and testing of the integrated float/sensor package is a joint effort led by LBNL and SIO. LBNL is responsible for calibration and data reduction.

*POC sensor*. Bishop (1999) and Bishop et al. (1999) demonstrated that beam attenuation coefficient at 660 nm is strongly correlated with particulate organic carbon (POC) in open ocean waters. Accurate and precise long-term high-frequency measurement of POC in the upper 1000 m requires the following: (1) a stable and precise transmissometer (beam attenuation stable to better than 0.001 $m^{-1}$), and (2) effective antifouling protection for transmissometer optics. Work on these issues is led by WETLabs.

*PIC sensor*. Particulate inorganic carbon occurs mostly as the mineral calcite and in most locations calcite is the dominant mineral in suspension. For this reason, we investigated optical properties (e.g. refractive index, birefringence...) specific to calcite that might be used to quantify PIC suspensions. LBNL is developing and proving the PIC sensor concept and WETLabs is implementing the PIC sensor concept in hardware and addressing biofouling issues.

## WORK COMPLETED

LBNL (in cooperation with WetLabs, Inc.) has initiated work on the design and implementation of sensors for particulate organic carbon (POC) and particulate inorganic carbon (PIC) on SOLO. The POC sensor development is well underway and sea trials of the sensor integrated with SOLO are scheduled for early November 2000 (see also SIO and WETlabs, reports). Chris Guay and Todd Wood have contributed substantially to this project at LBNL.

The PIC sensor concept was evaluated using a variety of optical approaches including scattering (Mueller matrix imaging) and simple light transmission measurements with crossed linear polarizers. Our tests with sand-sized amorphous/mineral phases quickly demonstrated the promise of using transmission for the detection of birefringence signal from calcite (Figure 1).

We used a bench-top spectrophotometer equipped with a 1-cm path length sample cell and modified with linear polarizers to measure the birefringence of suspended particles. Samples with PIC concentrations between 12.1 and 1820 µmol $CaCO_3$ $L^{-1}$ were prepared from a series of suspensions contain-

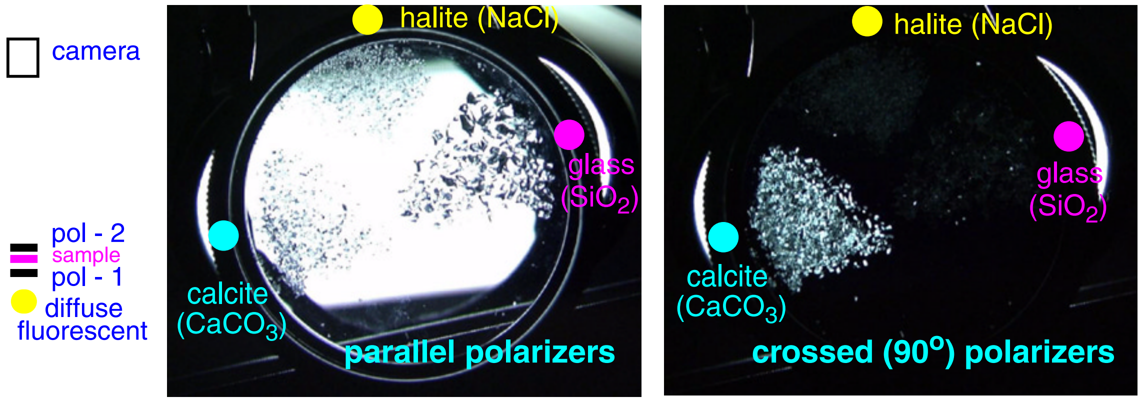


***Figure 1. Simple demonstration of calcite birefringence. Illumination of minerals and glass with transmitted fluorescent light; particles are sandwiched between linear polarizers. Images obtained using a CCD camera. Calcite is a strongly birefringent mineral; halite is a non-birefringent mineral; and glass is a non-birefringent amorphous solid. When polarizers are crossed, calcite particles light up.***

ing calcareous marine sediment material and varying amounts of non-birefringent diatomaceous earth powder. The $CaCO_3$ content of the suspensions ranged from < 1% to 95%, by weight. Birefringence signals were less than $10^{-3}$ of the incident beam strength but were readily detected.

A positive relationship was observed between birefringence and PIC, with sensitivity decreasing as the total particle concentration and the relative proportion of non-$CaCO_3$ particles in the sample increased. By applying a correction to the birefringence signal based on conventional (i.e., non-polarized) transmittance, the suite of analytical curves for the ≥ 32% $CaCO_3$ suspensions was reduced to a single linear relationship (Figure 2). The correction also linearized the analytical curve for the 9% $CaCO_3$ suspension, but its slope was 34% less than that of the more $CaCO_3$-rich suspensions.

A detection limit of ~0.3 µmol $CaCO_3$ $L^{-1}$ was determined based on the intrinsic signal noise (3σ) of the modified spectrophotometer and a 1 cm cell path-length. The precision of the method (2σ for replicate analyses) ranged from 1.3% to 6.5% of the blank corrected signal. This method can be used, without further modification, to quantify PIC in waters where concentrations are high and $CaCO_3$ is a major component of total suspended material (e.g., surface ocean waters during coccolithophore blooms). Our laboratory results defined performance requirements and design parameters (e.g., path length) for an *in situ* instrument capable of operating over the entire oceanic range of PIC.

We have further work on understanding the birefringence signals from mixed particulate matter suspensions but our spectrophotometer method can be used at sea without modification to quantify PIC systematics in ocean waters influenced by coccolithophore blooms.

WETLabs has constructed a propotype 10 cm pathlength in-situ instrument and it is undergoing evaluation at LBNL. We expect to have a working in-situ instrument by the time of our test cruise in November 2000.

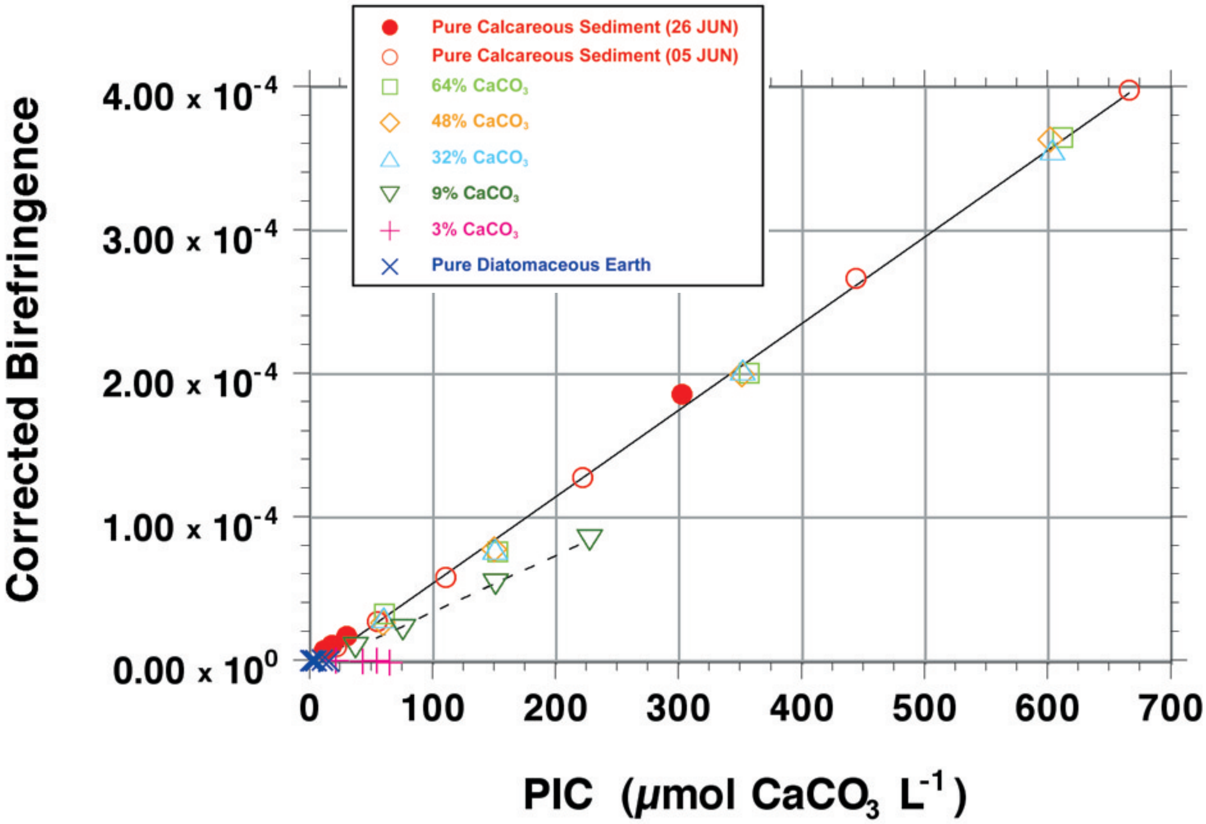


*Figure 2. Corrected birefringence for the serial dilutions of the suspensions containing mixtures of calcareous sediment and diatomaceous earth. Wave length 660 nm, pathlength = 1 cm. The solid line indicates the least-squares linear regression of corrected birefringence on PIC for the combined data from the pure calcareous sediment suspension and the mixed suspensions with $CaCO_3$ content ≥32%. The dashed line indicates the least-squares linear regression for the 9% $CaCO_3$ suspension.*

## RESULTS

PIC sensor development efforts are described in Guay and Bishop (2000- submitted) and will be presented at the Ocean Optics XV meeting in Monaco; a patent disclosure has been filed.

## IMPACT/APPLICATIONS

The sensors and methodology employed in this project can easily migrate to other autonomous platforms; furthermore, the work of this partnership will lay the foundation for expanded sensor suites and their integration onto recoverable autonomous self-navigating platforms designed to quantify both the reactants and products of photosynthesis, and the rates of carbon-system processes.

## TRANSITIONS

None as yet.

## RELATED PROJECTS

Russ Davis and Jeff Sherman (SIO) and Casey Moore (WETLabs) are supported separately by ONR under this National Ocean Partnership Program project.

Greg Mitchell (SIO) and Jeff Sherman are supported through the ocean optics program to instrument SOLO with radiance sensors. This instrument recently successfully completed a 76-cycle time series in the Japan Sea with good results. It will be desirable to eventually integrate these sensors with the POC and PIC sensor suite to make more comprehensive observations of the upper ocean carbon system.

## REFERENCES

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## PUBLICATIONS

Guay. C.K. and J.K.B. Bishop (submitted) A rapid birefringence method for measuring suspended $CaCO_3$ concentrations in water, Deep-Sea Research.

## PATENTS

Patent Disclosure: JIB-1595: Bishop, J.K.B. and C.K. Guay. An in-situ optical sensor for measuring particulate inorganic carbon in seawater.