



Ocean acidification: documenting its impact on calcifying phytoplankton at basin scales

William M. Balch^{1,*}, Victoria J. Fabry²

¹Bigelow Laboratory for Ocean Sciences, PO Box 475, W. Boothbay Harbor, Maine 04575, USA

²Department of Biological Sciences, California State University San Marcos, San Marcos, California 92096-0001, USA

ABSTRACT: In this paper, we evaluate several approaches to discern the impact of ocean acidification on calcifying plankton, over basin scales. We focus on estimates of the standing stock of particulate inorganic carbon (PIC) associated with calcifying plankton since it is thought that these organisms will be the most sensitive to ocean acidification. Chemical techniques provide the greatest accuracy and precision for measuring the concentration of PIC in seawater, but basin-scale chemical surveys are formidably expensive due to the high costs of ship time and analytical instrumentation. Optical techniques, while not yet as precise as chemical methods, provide the opportunity to rapidly sample over much greater spatial scales, with large numbers of samples contributing to each PIC determination (which reduces the SE of each mean determination). Optical measurements from autonomous platforms (buoys and gliders) will provide important depth resolution of PIC, which is otherwise not accessible to ocean color satellites. We propose a strategy for future PIC measurements that employs both optical and chemical measurements on the same water samples. This will ensure adequate knowledge of the PIC backscattering cross-section, critical for satellite PIC determinations at basin scales.

KEY WORDS: Coccolithophores · Ocean acidification · Calcium carbonate · Calcite · Coccolith · Ocean backscattering

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TIME AND SPACE CONSIDERATIONS OF OCEAN ACIDIFICATION

Ocean acidification resulting from anthropogenic CO₂ will likely take place over basin scales since anthropogenic CO₂ is globally dispersed throughout the atmosphere but with notable spatial bias (Conway et al. 1994). Moreover, the impact of ocean acidification will vary by latitude due to the low CO₃²⁻ concentrations in cold, polar waters as well as increased concentrations of CO₂ associated with recently upwelled water, also prevalent at high latitudes (Orr et al. 2005). Ideally, methods to study the impact of ocean acidification should match the global scale of its influence.

Sampling frequencies for detecting the impact of ocean acidification should be at least annual, in order to discern the complicating effects of other well-known climate phenomena such as El Niño that cause strong interannual variability in global weather patterns and

marine productivity. Seasonal aliasing also could be significant, however (e.g. due to temperature effects on CO₂ equilibrium as well as seasonal variability in phytoplankton primary production and community respiration). We could resolve seasonal variability with a sampling frequency of 8 times yr⁻¹, (i.e. the Nyquist frequency, the minimal frequency with which one could unambiguously represent the data without aliasing; Nyquist 1928).

By far, one of the biggest predicted biogeochemical effects of ocean acidification will be on the global ocean carbonate cycle. The global standing stock of particulate inorganic carbon (PIC) depends on calcium carbonate production and dissolution, both of which are expected to be affected by ocean acidification. In the pelagic ocean, PIC is contributed by a host of marine organisms, including: coccolithophores, calcifying dinoflagellates (e.g. *Thoracosphaera* sp.), foraminifera, pteropods, and diverse larval species of calci-

*Email: bbalch@bigelow.org

fyng invertebrates. The relative contribution of these groups varies in space and time, but on a global basis, coccolithophores are one of the most important producers of biogenic CaCO_3 .

The effect of climate change and ocean acidification on coccolithophores will be difficult to predict unequivocally. On the one hand, a lower pH and carbonate ion concentration might reduce calcification in the bloom-forming coccolithophores *Emiliana huxleyi* and *Gephyrocapsa oceanica* (Riebesell et al. 2000, Zondervan et al. 2002), but the response does not appear to be uniform across all coccolithophorid species (Langer et al. 2006). On the other hand, changes in climate (warming and precipitation) could enhance vertical density stratification, which is known to encourage *E. huxleyi* growth over other phytoplankton species such as diatoms (Tyrrell & Taylor 1996). The purpose of this essay is to discuss techniques for large-scale assessment of the impact of ocean acidification on the standing stock of suspended PIC, which is a good overall proxy of the ocean carbonate cycle. The chemical and optical methods we will discuss have been used primarily to assess small PIC particles such as coccolithophores and calcifying dinoflagellates. We will discuss the various methods and end by outlining an overall strategy for detecting basin-scale changes in PIC.

MEASURING THE STANDING STOCK OF PIC

Chemical techniques

The standing stock of PIC can be estimated over basin scales using chemical analyses of particulate calcium measured from ships. A number of techniques are available to estimate particulate calcium including X-ray fluorescence (Hurd & Spencer 1991, Twining et al. 2004), and atomic absorption (AA) (including flame AA, graphite furnace AA, and inductively coupled plasma AA [ICPAA]) (Cheng et al. 2004) or inductively coupled plasma mass spectrometry (ICPMS) (Platzner et al. 2008). Background seawater concentrations of calcium (~0.1 mM) present a challenge to measuring particulate calcium, since dissolved Ca^{++} in seawater must be rinsed away completely in order to accurately discern nanogram quantities of particulate calcium. This is usually accomplished by carefully rinsing filters with buffered potassium tetraborate tetrahydrate (Fernández et al. 1993). Moreover, with AA, corrections for background seawater can be made by simultaneous measurement of sodium. Profiles of particulate calcium made using AA have shown excellent precision and consistent decreases in particulate calcium concentrations with increasing depth over the top 500 m

(Sherrell et al. 1998), suggesting removal of PIC particles (see also Bishop et al. 1980, 1986). Such chemical observations, along with a plethora of other evidence, have led to the speculation that calcium carbonate particles are dissolving above the lysocline (Milliman et al. 1999).

Chemical techniques such as ICPAA, ICPMS, and even X-ray fluorescence are highly accurate and precise for measuring particulate calcium, yet seasonal, basin-scale ocean surveys, such as WOCE (World Ocean Circulation Experiment)- or GEOSECS (Geochemical Ocean Section Study)-style decadal surveys, would be prohibitively expensive using such techniques. It should be noted that, unless a large volume of water is sampled for particulate calcium, relatively large, rare PIC particles from foraminiferal tests, pteropod shells, and calcareous invertebrate larvae may be undersampled. This highlights an advantage of high-volume, *in situ* filtration units (Bishop et al. 1985, Thomalla et al. 2008). Nevertheless, distinct advantages of the chemical techniques are the accuracy and precision associated with the laboratory analyses and the high resolution of vertical profiles of PIC. It should be noted, however, that compared to particulate organic carbon, relatively few data exist on the vertical distribution of PIC (Bishop et al. 1980, Balch & Kilpatrick 1996, Sherrell et al. 1998, Balch et al. 2000, Poulton et al. 2006) and chemical techniques remain the most accurate way to quantify PIC.

Optical measurements on small volumes

Optical approaches for estimating PIC are based fundamentally on the strong refractive index of calcium carbonate relative to water (1.19) (Broerse et al. 2003), which is significantly greater than relative refractive index of pure biogenic silica (1.06) (Costello et al. 1995) or non-minerogenic phytoplankton (1.05 to 1.06) (Ackleson & Spinrad 1988). The high relative refractive index means that calcium carbonate is an intense scatterer of light. Calcium carbonate also is highly birefringent (it rotates the plane of polarized light by 90°), a property used by micropaleontologists for decades to enumerate biogenic and lithogenic mineral particles (Fig. 1A).

Recently, a technique to document particle birefringence has been adapted to estimate PIC by adding polarizing filters to a transmissometer (Guay & Bishop 2002). It is calibrated using purified mineral suspensions of diatomaceous earth and calcareous sediments. The technique shows promise. One possible limitation is that other organic molecules also can be highly birefringent. For example, in observations of thousands of samples with polarization microscopy, we have observed that zooplankton carapaces, certain

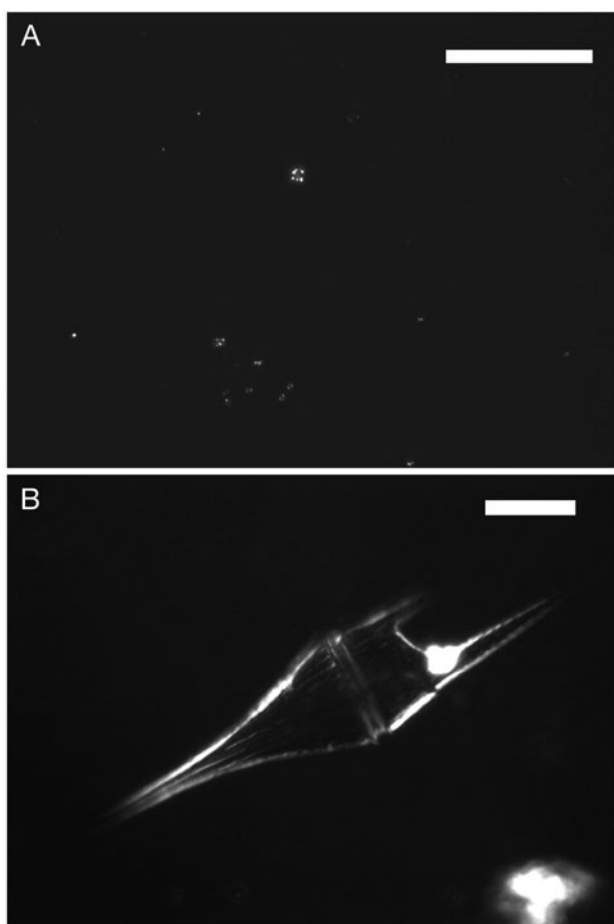


Fig. 1. (A) Birefringence microscopy image of detached coccoliths and plated coccolithophores of various species taken from the north Atlantic Ocean (30.462°N, 19.467°E; 2 m depth) on 26 September 2004 during Atlantic Meridional Transect cruise 15 aboard the RRS 'Discovery'. The technique for preparation of the sample was according to Haidar & Thierstein (2001). Scale bar = 30 μ m. Micrograph was made using 1.00 s exposure time. (B) Birefringence microscopy image of a dinoflagellate of the genus *Ceratium* taken from the north Atlantic Ocean (45.599°N, 20.275°E; 5 m depth) on 26 June 2005 during Atlantic Meridional Transect cruise 16 aboard the RRS 'Discovery'. Slide preparation same as in (A). Scale bar = 30 μ m. Exposure time was 1.34 s. All other settings identical to those used for the image in (A). Panel (B) is presented as an example of a non-calcifying cell that is birefringent. Birefringent organic debris is relatively common in natural samples, thus the presence of such particles must be included in the calibration of the birefringence technique for particulate inorganic carbon (PIC) quantification

dinoflagellate thecae, as well as generic detritus can be birefringent (e.g. Fig. 1B). This would mean that in field samples, organic detritus could potentially lower the accuracy of birefringence-based PIC estimates. Nonetheless, provided the above transmissometer technique is calibrated with suspensions of naturally occurring particles (including naturally occurring PIC

and organic detritus), such errors should be easily quantifiable. This technology has been adapted for use on autonomous drifters (Bishop et al. 2004), which provides useful information on the standing stock of PIC over the entire water column and at mesoscale spatial domains, over periods of days to months. It would be especially useful for quantifying PIC in coccolithophore blooms.

Optical backscattering of PIC can also be used to estimate the standing stock of PIC. Acid-labile backscattering represents the backscattering that disappears following the lowering of seawater pH to <5.8. This technique lends itself to semi-continuous measurements aboard ships, in which backscattering and pH are measured continuously in seawater from the ship's non-contaminated seawater system. Every 2 min, the pH is lowered using a weak acid to dissolve PIC. Once the pH stabilizes at the lower value, optical backscattering is re-measured with a light-scattering photometer (which samples the optical volume scattering function). The difference between total and acidified backscattering measurements represents 'acid-labile backscattering', b_b' . By using the same photometer for acidified and unacidified measurements, this eliminates inter-instrument calibration issues and causes only minor spatial aliasing in the b_b' measurement (Balch et al. 2001).

The spatial resolution of this method, at typical ship speeds, is about 1 km, the same resolution as satellite ocean color measurements. Adding a second sensor (one for raw seawater and one for constantly acidified seawater) would allow this spatial scale to be reduced further, but at the expense of increased errors due to sensor inter-calibration. Estimates of b_b' can be calibrated to PIC concentration as a power function, which typically explains about 77 to 85% of the variance in PIC concentration, in non-bloom and bloom waters alike (Balch et al. 2001). Drops in the explained variance can be attributed to differences in particle backscattering cross-section for different-sized calcium carbonate particles (Balch et al. 1999).

Optical techniques and remote sensing

While optical scattering by PIC occurs in all directions (forward and backward), it is the strong backward scattering (b_b) of PIC that is critical to its being remotely sensed from space (Gordon et al. 1988). Remote sensing reflectance at a given wavelength, λ , is a function of both absorption, $a(\lambda)$, and backscattering, $b_b(\lambda)$, and varies as $b_b(\lambda)/a(\lambda)$. Coccolith PIC has barely measurable absorbance (Balch et al. 1991), thus the presence of PIC principally elevates b_b , thus increasing reflectance.

One complication in the optical remote sensing of PIC is that the relationship between $b_b(\lambda)$ or total integrated scattering ($b(\lambda)$) versus PIC concentration is not necessarily the same for different-sized PIC particles. For example, optical scattering per unit PIC (otherwise known as the scattering cross-section, b^* , in units of $\text{m}^2 (\text{mol PIC})^{-1}$) is orders of magnitude lower for a large particle like a pteropod than for a small coccolith (Balch et al. 1996). Moreover, the backscattering cross-section, b_b^* , shows moderate variability between different species of coccolithophores (Balch et al. 1999). This means that enhanced backscattering in the ocean caused by PIC is mostly due to small PIC particles like coccoliths and is negligible for larger particles such as foraminifera and pteropods. Moreover, this illustrates an important limitation of optical PIC determinations (whether based on scattering or birefringence) since the scattering cross-sections of small coccoliths are not constant but have some degree of variability, and layering of coccoliths, such as around cells, can cause nonlinear variability in their volume-scattering properties.

Information on the backscattering cross-section of field PIC particles has been critical for development of a coccolithophore remote-sensing algorithm, which is fundamentally a backscattering algorithm (Gordon et al. 2001, Balch et al. 2005) (Fig. 2A). These algorithms are not just for high-reflectance coccolithophore blooms but can be used in non-bloom situations as well. While remote-sensing algorithms for PIC are less precise than chemical PIC measurements, regional and temporal binning of satellite data allows time/space averages to be calculated with estimated SEs well below the concentration of PIC in seawater (e.g. the SE for 36 km, monthly binned data is 6.67 nM PIC; Balch et al. 2005). A frequency plot of ship and satellite-derived PIC concentration demonstrates similar concentration ranges in the Atlantic Ocean from 50° N to 40° S (Fig. 2B). Plots of satellite-derived PIC concentrations versus ship-based values are highly statistically significant ($p < 0.001$), although they account for only about 63% of the total variance for a linear fit (SE: 0.069 μM) or 25% of the total variance for a power fit (SE: 0.33 log units) (Fig. 2C). This result is to be expected, especially in oligotrophic waters in which there are other particles that affect the average background backscattering. In coccolithophore blooms, the relative precision of the PIC determination is higher due to the fact that PIC dominates all other particle backscattering (increased signal-to-noise ratio).

Along-track comparisons of satellite versus ship-derived PIC concentrations show regions of consistent satellite bias (Fig. 2D,E) probably associated with differences in water mass and particle types and mean changes in the background backscattering. Recent

empirical algorithms also have been developed to estimate coccolithophore calcification from satellite, based on sea surface temperature, chlorophyll, PIC, day length, and depth (Balch et al. 2007). Determination of both PIC standing stock and production rate allows the estimation of PIC turnover times, which are relatively fast, typically on time scales of ~5 d (Balch & Kilpatrick 1996, Balch et al. 2000, Poulton et al. 2007).

Another complication to remote sensing of PIC is that most of the reflectance from the surface ocean originates from the top 2 optical depths of the euphotic zone (i.e. waters above the depth where irradiance exceeds 13.5% of surface irradiance) (Gordon & McCluney 1975). Indeed, the reflected light emanating from the sea is heavily weighted to the top optical depth (i.e. water above the depth of 37% irradiance penetration). Phytoplankton inhabit the euphotic zone, usually defined as the zone where irradiance is $\geq 1\%$ of surface irradiance. Since light diminishes exponentially with depth, the euphotic zone encompasses 4.6 optical depths ($\ln(0.01) = -4.6$). Thus, passive remote sensing techniques only 'see' the surface depths of the euphotic zone, and miss the deeper phytoplankton populations. This suggests that *in situ* measurements (whether from glider, buoys, or ships) will be important for resolving the deep PIC not discernible from satellite. It should be noted, however, that despite this restriction of satellite optical measurements to the top optical depths, satellite images of surface phytoplankton chlorophyll have consistently demonstrated remarkably coherent, basin-scale distributions, over time scales of days to years (McClain et al. 2004). Such rapid evaluation of surface phytoplankton variability across the globe can only be achieved through satellite remote sensing.

A STRATEGY FOR THE DETECTION OF LONG-TERM, BASIN-SCALE VARIABILITY IN PIC

Chemical and optical techniques for measuring PIC have important biases. Chemical measurements allow better depth resolution, but they require labor-intensive, ship-based sampling. This limits the numbers of samples that can be taken, thereby limiting the spatial resolution and frequency of sampling. Optical estimates have the advantage of large sample sizes and rapid sampling frequency, but lower precision and limited depth resolution. The latter will require deep *in situ* measurements or statistical modeling of the PIC profile, just as others have modeled the relationship between surface chlorophyll and integrated chlorophyll for the determination of euphotic-zone phytoplankton biomass (Morel 1988, Platt et al. 1988, Balch et al. 1992). Similarly, Mitchell (1996) found that chlorophyll algorithms had to

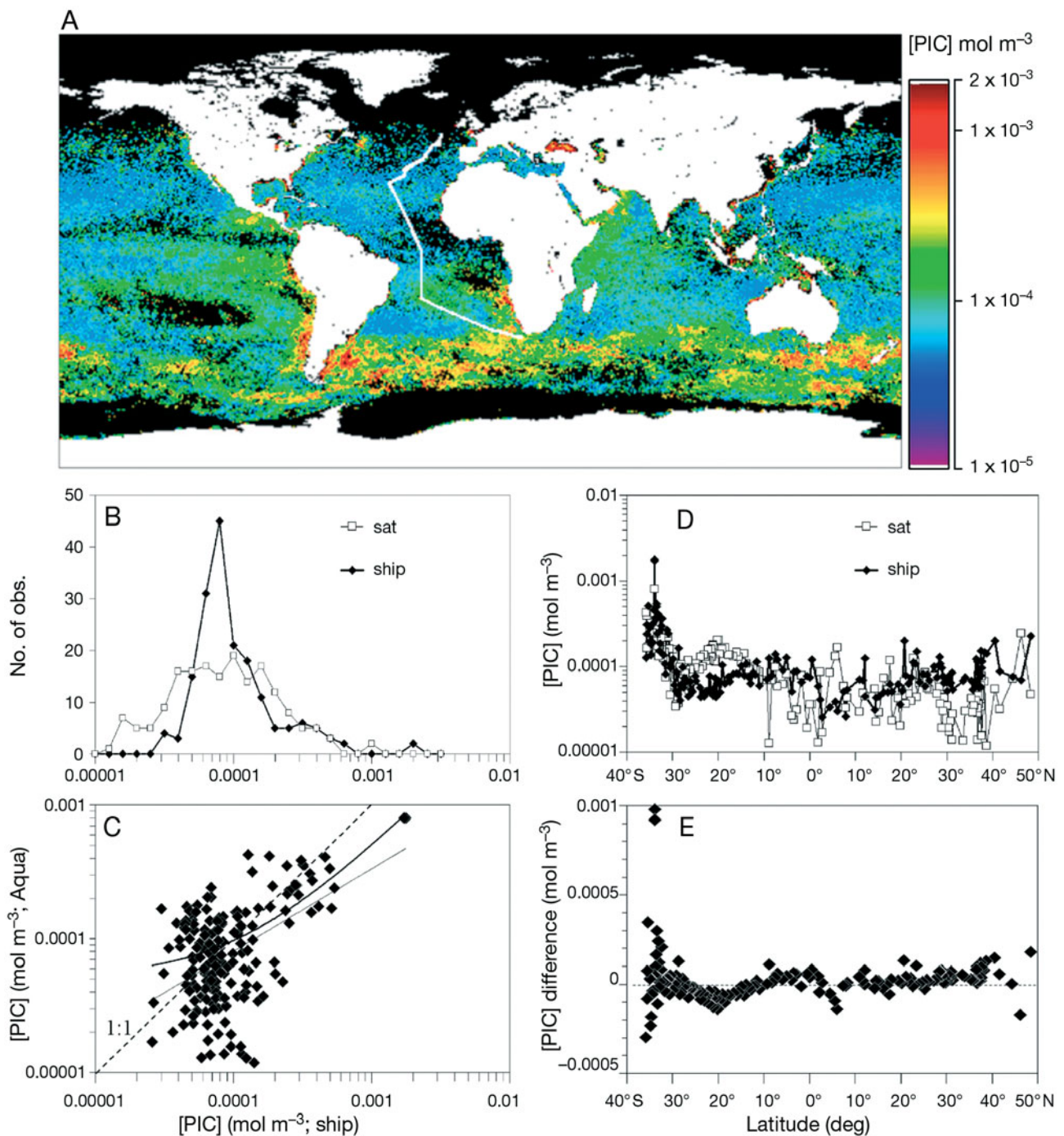


Fig. 2. (A) Global monthly MODIS-Aqua composite image of particulate inorganic carbon (PIC) concentration for November 2005, as determined using the merged 2-band/3-band PIC algorithm (Gordon et al. 2001, Balch et al. 2005). Color bar for PIC concentration shown on right side. Transect of Atlantic Meridional Transect cruise 17 (50°N to 40°S) aboard the RRS 'Discovery' shown as white line. (B) Frequency plot of PIC concentration values for both ship (◆) and satellite (□) measurements. Results demonstrate similar overall distributions; median values differ by 0.9% (satellite greater), average values differ by 16% (ship greater) and the modes differ by 11% of each other (ship greater). SDs of the data distributions are 0.375 log units for the satellite results and 0.302 log units for the ship data. (C) Monthly-binned satellite-derived PIC values plotted against surface PIC values measured aboard ship. Dashed line represents the 1:1 relationship. Bold upper line represents the best-fit line ($y \pm 6.94 \times 10^{-5} = 0.4548 \pm 0.026 x + 5 \times 10^{-5} \pm 6.2 \times 10^{-6}$; $r^2 = 0.63$; $F = 295$; $p < 0.001$). Lower fine line represents the best-fit power function ($y \pm 0.326 = 0.0237 \pm 0.0199 x^{0.6173 \pm 0.0816}$; $r^2 = 0.25$; $F = 57$; $p < 0.001$). Equation values in square brackets are the SEs of each preceding coefficient. (D) PIC concentration as a function of latitude. Symbols as in (B). (E) Difference in PIC concentration (ship-satellite) shown in (D), as a function of latitude

be adjusted for geographic variability in the absorption cross-section of chlorophyll, and likewise, PIC algorithms may have to incorporate the variability in the PIC-specific backscattering cross-sections in different parts of the global ocean. Insufficient data currently exist to resolve whether there are coherent trends in b_b^* in space and time in the sea, but such trends, if they exist, would provide invaluable information for the global remote sensing of PIC. This information will be critical for assessing whether coccolithophores are changing their geographic distribution as a function of ocean acidification.

To document the effect of ocean acidification on the global carbonate cycle, methods are needed to accurately extrapolate point measurements over basin scales. We believe that the best strategy will involve a combined chemical and optical approach, using multiple platforms. That is, time-series sites should routinely measure PIC profiles using both chemical and optical techniques. Chemical techniques will provide accurate estimates of PIC standing stock (highly temporally resolved but spatially limited). Such measurements would probably be done aboard ships. Parallel optical analysis of PIC in the same shipboard water samples will provide the information needed to calibrate optical PIC algorithms (whether for in-water or satellite-derived optical measurements).

Ships and fuel are increasingly expensive and other platforms should be considered in this strategy such as profiling buoys (Argo Science Team 1998, Alverson & Baker 2006) and gliders (Schofield et al. 2007); gliders can extend long-term coverage of the ocean, on time scales of months, spatial scales of 500 to 1000 km and depth scales of thousands of meters. Profiling floats have been successfully equipped with optical instrumentation (Son et al. 2006, Boss et al. 2008) as well as instrumentation to estimate particulate organic carbon (Bishop et al. 2004). Outfitting floats with PIC birefringence sensors (Guay & Bishop 2002) or acid-labile backscattering sensors (Balch et al. 2001) should be straightforward, provided that there is a robust field calibration. Gliders are now available 'off the shelf', equipped with highly sophisticated radiometers, absorption, and backscattering sensors. Fundamentally, the critical link to interpret PIC data from autonomous platforms will be the quality of the calibration between PIC concentration and optical properties.

While PIC remote sensing only works for the smallest calcite particles (i.e. coccolithophores and coccophores), standing stock measurements of PIC associated with foraminifera and pteropods will be critical for understanding the other major components of the global PIC standing stock. Observations of these heterotrophic organisms will have to extend much deeper than the euphotic zone due to their wide-ranging

depth preferences and will require sampling methods and volumes appropriate for their larger sizes and typically lower concentrations in sea water, relative to coccolithophores.

NEW DEVELOPMENTS

There are some new developments for documenting the carbonate cycle over large spatial scales. Techniques for measuring the inorganic carbon system in seawater (e.g. total alkalinity, dissolved inorganic carbon concentration, $p\text{CO}_2$, and pH) have improved sensitivity, accuracy, and precision (DeGrandpre et al. 2002, Nemzer & Dickson 2005, Martz et al. 2006, Seidel et al. 2006), and the availability of certified reference materials (CRMs) has been critical to achieving high-quality, reproducible measurements (Lamb et al. 2001, Sabine et al. 2002a, Chung et al. 2003, Dickson et al. 2003). *In situ* PIC dissolution rates have been estimated by combining total alkalinity increases (corrected for the effect of salinity and nitrate) in a water parcel with age estimates obtained from chlorofluorocarbon (CFC-11 and CFC-12) concentrations or carbon-14 ages (for deeper waters where CFC-11 and CFC-12 were not detectable) (Feely et al. 2002, 2004, Chung et al. 2004, Berelson et al. 2007). Specific details of this calculation can be found in Feely et al. (2004). Such alkalinity-derived estimates of PIC dissolution in the upper ocean, which integrate over large spatial and temporal scales, suggest that the aragonite and calcite saturation horizons in several regions are shoaling as a result of oceanic uptake of atmospheric CO_2 (Feely et al. 2002, 2004, Sabine et al. 2002b, Chung et al. 2003, 2004, Berelson et al. 2007) and the reported increase in alkalinity (Sarma et al. 2002) implies that enhanced dissolution of PIC particles has already occurred. While the areas of undersaturation with respect to aragonite and calcite appear to be expanding in several areas (Feely et al. 2004), there is currently no long-term monitoring effort to track and quantify PIC dissolution fluxes. Because increased PIC dissolution in the upper water column enhances the ability of the oceans to absorb anthropogenic CO_2 , it is an important feedback in the carbon cycle.

There are 2 recent optical advances worthy of note. One new development is the use of range-gated light detection and ranging (LIDAR) techniques for understanding the vertical distribution of optically scattering particulate matter throughout the euphotic zone. This has been accomplished from aircraft (Chekalyuk 2006, Cowles et al. 2006) and more recently from satellite sensor (Koziana et al. 2006, Y. Hu pers. comm.). While the technology is still young, such

measurements will add the depth dimension to remotely sensed PIC measurements, thereby providing the means to directly measure backscattering over the water column and vertically integrate PIC instead of relying on statistical information to extend surface measurements to depth.

Another new development concerns the multi-angle imaging spectroradiometer (MISR) instrument on board the NASA Terra satellite platform. This instrument measures radiance at 9 different angles (-70° to 70° from nadir), at 4 bands (blue, green, red, and near-infrared), in a narrow, 250 km swath, and with a 9 d global repeat time. While it is primarily designed to look at atmospheric properties, with careful atmospheric correction, it can be used to examine whether the reflectance coming from the sea surface is isotropic (the same in all directions). There is some preliminary evidence (J. Martonik & D. Diner pers. comm.) that MISR can detect differences in the angular dependence of reflectance associated with turbid coccolithophore blooms versus non-coccolithophore dominated waters. Certainly laboratory evidence based on optical volume-scattering measurements in coccolithophore cultures (Voss et al. 1998) verified that the volume-scattering function of coccolithophores is flatter in the backwards direction. It is not known whether the space-based observation of more isotropic backwards scattering in a coccolithophore bloom is true for all phytoplankton or is unique to coccolithophores. This clearly deserves more work.

CONCLUDING REMARKS

A combination of in-water (i.e. ship, autonomous vehicle, buoy) optical and chemical measurements, plus satellite optical measurements, will be needed to fully discern the effect of ocean acidification on the standing stock of PIC, across ocean basins, and over seasonal to decadal time scales. Such results will be important for modeling the ocean biosphere, albedo (Tyrrell & Taylor 1996, Tyrrell et al. 1999), and DMS production (Malin et al. 1993, Matrai & Keller 1993), just to name a few examples. Chemical observations of PIC will remain key for the documentation of ocean acidification, particularly through global-scale research programs (like WOCE or GEOSECS). 'Decadal repeat' chemical measurements of PIC will accurately assess long-term change in the carbonate cycle associated with ocean acidification. Estimation of basin-scale changes in the carbonate cycle over sub-decadal time scales, however, will best be achieved through dedicated optical sampling with autonomous buoys (e.g. the ARGO program; Balmaseda et al. 2007) and ocean color satellites.

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