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Aerial extent, composition, bio-optics and biogeochemistry of a massive under-ice algal bloom in the Arctic

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Running head: Carbon fixation and composition of an under-ice algal bloom

Abstract

It has been long thought that coccolithophores are a minor component of the phytoplankton assemblage in Arctic waters, with diatoms typically being more dominant. Little is known about how the phytoplankton communities will change, however, as the Arctic warms. We participated in the 2011 ICESCAPE (Impacts of Climate on EcoSystems and Chemistry of the Arctic Pacific Environment) cruise to the western Arctic, performing a combination of
discrete measurements (microscopy, calcification, particulate inorganic carbon (PIC), particulate organic carbon (POC), biogenic silica (BSi) plus continuous surface bio-optical measurements (absorption, scattering, backscattering and acid-labile backscattering; the latter specific for coccolithophores). Here, we report bio-optical and coccolithophore observations from the massive under-ice algal bloom originally described in Arrigo et al. (2012). The most intense portions of the bloom were centered in cold Winter Water and there was evidence for nitrate drawdown in the top 10-20m with strong penetration of silicate rich water into the surface waters. Surface chlorophyll $a$ and particulate absorption at 440nm approached 30$\mu$g L$^{-1}$ and 1.0 m$^{-1}$, respectively. Particulate absorption of detritus ($a_p$ at 412nm) was highly correlated to $a_p$ at 440nm associated with chlorophyll $a$ and slopes of the absorption spectrum showed that both dissolved and particulate absorption at 412nm exceeded that at 440nm, with slopes, $S_g$, of 0.01. Colored dissolved organic matter fluorescence (FDOM) was high in the bloom but the relative fluorescence yields were low, characteristic of phytoplankton-produced FDOM (as opposed to terrestrially-produced FDOM). Coccolithophore backscattering was elevated in the under-ice bloom, but it only accounted for 10% of the total particle backscattering, relatively low compared to typical subpolar waters further to the south. Total particle scattering was significantly elevated in the under-ice bloom (values of almost 2 m$^{-1}$), likely due to the high abundance of large diatoms. Backscattering probabilities in the bloom were $\sim$1%, again characteristic of diatom-dominated populations with few calcifiers. PIC standing stock in the under-ice bloom was low but measurable while biogenic silica molar concentrations were 150 times greater. POC:PON molar ratios were 6-10, characteristic of healthy, rapidly growing phytoplankton, observations further buttressed by carbon:chlorophyll mass ratios of 50-100. Coccolithophore calcification was low but measurable, reaching 1.75mg C m$^{-3}$ d$^{-1}$ in the under-ice bloom, only 0.4% of the photosynthesis. However, the intrinsic carbon-specific
growth rate was 0.4 per day for bulk POC and ~1 per day for bulk PIC, close to maximal growth rates expected at these temperatures. SEM and light microscopy results showed mostly diatoms in the bloom. The coccolithophore, *Emiliania huxleyi*, was observed, providing unequivocal evidence of the presence of coccolithophores in the under-ice algal bloom.

1 Introduction

1.1 Polar phytoplankton and coccolithophores

Arctic waters have long been characterized by strong diatom dominance, as evidenced in the first description of diatoms in Arctic sea ice (Ehrenberg, 1841) as well as more recent accounts (Bursa, 1961; Poulin *et al*., 2011; Saito and Taniguchi, 1978; von Quillfeldt, 2000) that show diatoms to be the significant drivers of Arctic primary production in the upper water column (and under ice). Dinoflagellates are also regularly seen in Arctic waters but at lower biomass than the diatoms (Braarud, 1935; Horner, 1984; Poulin *et al*., 2011).

*Phaeocystis* is another common phytoplankter in Arctic waters (Poulin *et al*., 2011; Sherr *et al*., 2003) as are nanoflagellates, which can contribute the majority of carbon biomass at specific times (Sherr *et al*., 2003).

Relative to the other phytoplankton groups, coccolithophores have traditionally been thought to be rare (or absent) in Arctic waters (Poulin *et al*., 2011) and more abundant in the sub-polar, temperate, sub-tropical and tropical biogeographic zones of the world ocean (McIntyre and Be, 1967; Okada and Honjo, 1973; Winter *et al*., 1994; Ziveri *et al*., 2004). One hypothesized reason for the low abundance of coccolithophores in polar waters has been that they typically show lower growth at temperatures <8°C and in reduced solar radiation (Raitsos *et al*., 2006), such as in polar waters.

Despite their typically low abundance, coccolithophore blooms have been observed in ice-free polar waters using space-based remote sensing. Evidence from the AVHRR
(Advanced Very High Resolution Radiometer) satellite, suggests that the frequency of
coccolithophore blooms in sub-polar and non-ice-covered polar Arctic waters has been
increasing over twenty years (Smyth et al., 2004). These blooms are probably Emiliania
huxleyi but it has been impossible to confirm this due to lack sea-truth data. Polar
coccolithophore species besides E. huxleyi were previously described in early taxonomic
studies from Resolute Bay (Northwest Passage), West Greenland and South Alaska (genera
Pappomonas, Wigmamma, Turrisphaera and Papposphaera) where the water temperature
was below 0°C (Manton et al., 1976a; Manton et al., 1976b; Manton et al., 1977). Recent
work in the Atlantic Arctic (partially ice-covered/ice edge region north of Svalbard)
demonstrated low abundance of coccolithophores (2.5 cells mL⁻¹) with species mostly from
the family Papposphaeraceae, found in waters <0°C with sub-micromolar nitrate and
phosphate (Charalampopoulou et al., 2011). Coccolithophore species observed in this same
study included E. huxleyi, Coccolithus pelagicus, Pappomonas sp., Papposphaera arctica
and Wigmamma sp.

1.2 Arctic primary production and calcification

There is relatively little information on blooms of algae under Arctic ice, primarily
due to the high reflectance of sea-ice, and the inability to see such blooms using satellite
remote sensing. Observations from ships have provided some evidence that blooms can
occur, however. For example, at ice station SHEBA in the western Arctic, chlorophyll
concentrations reached as high as 4.3 mg m⁻³ under the ice during the summer melting of
snow overlying the ice (Sherr et al., 2003). Typically, under-ice primary productivity has
been assumed to be low due to the strong attenuation of light by ice and snow. Hill et al.
(2013) and Matrai et al. (2013), examined historical ^14C primary production and chlorophyll
data. Surface productivity rates from regions like the northern Chukchi Sea were typically
<10 mg C m⁻³ d⁻¹ (Hill et al., 2013; Matrai et al., 2013). Nitrate also is seasonally drawn-
down under the ice, the extent of which can be used to estimate annual primary production (assuming a Redfield ratio of C:N in particulate matter and an f ratio of nitrate utilization) (Codispoti et al., 2012; Eppley and Peterson, 1979). Such estimates are within a factor of two of $^{14}$C measurements of net primary production (Codispoti et al., 2012; Hill et al., 2013).

Elevated integrated primary productivity has been documented in waters with >90% ice, with rates as high as 60 mg C m$^{-2}$ d$^{-1}$ (but after snow is removed from the ice) (Gosselin et al., 1997).

There is only one previous study of coccolithophore calcification in a partially ice-covered region north of Svalbard (Charalampopoulou et al., 2011). In an ice-free fjord and the marginal ice zone, calcification was low, with a subsurface peak of 0.02-0.07 mg PIC m$^{-3}$ d$^{-1}$. In a partially ice-covered region, calcification showed a subsurface peak of 0.6 mg PIC m$^{-3}$ d$^{-1}$ (Charalampopoulou et al., 2011). Such rates are extremely low compared to rates measured in more coccolithophore-rich, lower latitude waters (Balch et al., 2007).

The goal of this study was to use a combination of continuous underway and discrete seawater measurements to document under-ice algal features during the ICESCAPE (Impacts of Climate on EcoSystems and Chemistry of the Arctic Pacific Environment) cruise to the western Arctic Ocean, July-August 2011. Moreover, we documented the hydrographic, biological and optical properties of these features and used the data to better understand: bloom magnitude, bloom size, dominant species, pigment-specific absorption, particle scattering and distribution of colored dissolved organic matter (CDOM). Discrete samples provided estimates of the standing stocks of particulate organic carbon (POC), particulate inorganic carbon (PIC), biogenic silica (BSi) plus photosynthesis and calcification rates. These observations provide a baseline for interpreting future changes in the phytoplankton standing stocks, rates and bio-optical properties of the Western Arctic as the region undergoes climate change (Arrigo et al., 2008).
2 Methods

2.1 Cruise details

The ICESCAPE 2011 expedition took place in the western Arctic (Fig. 1A) aboard the USCGC Healy (cruise #1101) departing Dutch Harbor, AK, USA on 25 June and returning to Seward, AK on 29 July 2011. A total of 173 stations were sampled during the cruise which included 9 sea ice stations. The station domain extended from the coast of Alaska westward to the US-Russian border – and between the Bering Strait and ~74°N. The work presented in this communication is focused on a portion of the cruise track of Healy 1101, from the Alaskan coast to the region of the giant under-ice algal bloom, northwest of Barrow, AK, within the region 71°N to 74°N and 158.5°W to 169°W (stations 37-123 and 157-173) (Arrigo et al., 2012). Station numbers and their location are shown in Fig. 1B.

Measurements included running a continuous underway system (focused on hydrographic and bio-optical properties) and measuring discrete water samples for a variety of biological and biogeochemical variables. CTD stations typically involved sampling water from eight depths. Of those eight bottles, seven were usually from the euphotic zone and one from deeper in the water column. We also sampled the top Niskin bottle of numerous CTD casts for calibration samples for the continuous underway system.

2.2 Underway bio-optical system

The Balch lab bio-optical underway system was run continuously over the course of the trip. It was started on 26 June, 2011 and shut down on 27 July, 2011 with shutdowns for weekly cleaning and calibration (see Section 2.3). This system has been described elsewhere (Balch et al., 2008). Briefly, the seawater source was located at 5m depth on CSCGC Healy. Water flowed through an ice separator then through insulated stainless steel pipes to the shipboard laboratory. Our flow-through system measured temperature, salinity, chlorophyll
a fluorescence, CDOM fluorescence (FDOM) and particle backscattering. Temperature and salinity were first measured with a SeaBird flow-through temperature and conductivity sensor. A WETLabs WETStar CDOM fluorometer was used to measure the fluorescence of colored dissolved organic matter (excitation = 370nm; emission = 460nm). This was plumbed into the flow path just after the temperature/salinity sensors. Next, chlorophyll fluorescence was measured with a WETLabs WETStar chlorophyll fluorometer (excitation = 460nm; emission = 695nm). Particle backscattering at 531 nm (using a WETLabs ECOVSF sensor aimed into a specially-designed container which minimized wall reflectance, hence maximizing the light scattering signal associated with marine particulate matter). First, the system measured particle backscattering of 531 nm light with raw seawater (pH≈8.1) running through the system for one minute. After 60 seconds of data collection (or whatever time period was set in order to have sufficient sample size to achieve standard errors of 0.5x10^{-5} m^{-1}), the acid controller injected 0.2 µm-filtered, 10% glacial acetic acid into the seawater stream, passing through a mixing coil to thoroughly mix it with the seawater, upstream of the ECOVSF. This reduced the pH to 5.5, below the dissociation point for various mineral forms of calcium carbonate. A pH sensor downstream of the sample chamber measured the pH constantly. Once the pH dropped to 5.5, backscattering was re-measured for an equivalent period of time after which the acid additions stopped and the pH re-equilibrated to raw seawater values and the entire cycle repeated. The difference in backscattering between raw seawater and acidified seawater represented “acid-labile backscattering” (b_{sl}), which can be directly related to the concentration of suspended calcium carbonate (Balch et al., 1996).

The underway bio-optical system had a separate flow loop that passed through a WETLabs ac-9, to measure spectral absorption and attenuation at nine wavelengths: 412, 440, 488, 510, 555, 630, 650, 676 and 715nm. In the flow path to the ac-9 was a solenoid
that diverted the seawater stream through a 1µm filter, then a 0.2 µm filter prior to running the water through the ac-9. Every two minutes, the solenoid would alternate between filtered and unfiltered seawater, thus providing absorption and attenuation (at 9 spectral wavelengths across the visible spectrum) for raw and filtered seawater. In turn, this allowed calculation of the absorption and attenuation of total suspended particles and dissolved organic matter. The difference between raw and dissolved ac-9 measurements represented particulate absorption and beam attenuation. Total scattering was calculated as attenuation minus absorption.

2.3 Underway system calibration

Calibrations of the complete underway system were performed just prior to departure, approximately weekly during the cruise as well as a final calibration after final shut down. These calibrations were used to estimate biofouling corrections during each operation period. The protocol was to run 0.2um filtered RO water from the ship’s Milli-Q system, under pressure, through the entire flow path prior to cleaning (“a dirty calibration” which provided the endpoint for estimating the optical contribution of biofouling). Then, the system was carefully disassembled and cleaned, reassembled and a “clean calibration” performed (which represented the beginning calibration for the next operational segment, with no biofouling. Post cruise, the biofouling corrections were interpolated between the initial clean calibration and the following “dirty calibration”. The backscattering signal associated with the wall of the flow-through container was also estimated by running 0.2um-filtered RO water following cleaning as well as 0.2um-filtered seawater. Daily, biofouling of the wall was estimated by first shunting the inflowing water through a separate 0.2um filter prior to passage through the system and comparing this b_{0pf} value to that of pure seawater (Mobley, 1994).

2.4 Discrete samples

For the full CTD cast (the “productivity cast”), particulate inorganic carbon (PIC) was measured on 0.2L seawater samples filtered onto 0.4µm pore-size polycarbonate filters,
rinsed with potassium tetraborate buffer (Poulton et al., 2006) and biogenic silica (BSi) was measured by filtering 0.2 L seawater onto 45mm 0.4μm polycarbonate filters, stored and measured according to Brzezinski et al. (1989). Particulate organic carbon (POC)/particulate organic nitrogen (PON) was measured using JGOFS protocols (JGOFS, 1996) while coccolithophore counts were processed ashore using polarized light microscopy (Haidar and Thierstein, 2001) (but substituting Norland #74 brand optical adhesive instead of Canada Balsam). Surface and chlorophyll maximum depths were sampled for scanning electron microscope and prepared for analysis ashore according to Goldstein et al. (2003). These same depths were sampled for “live” microscopy using the Filter Freeze Transfer technique (Hewes and Holm-Hansen, 1983), with samples filtered on 0.4μm polycarbonate filters prior to transfer and then samples examined using an AO-Spencer Model 10 microscope equipped with epifluorescence and polarization optics. Nutrient samples were run on an AA3 autoanalyzer for nitrate, nitrite, ammonium, phosphate and silicate (but only nitrate and silicate results will be discussed here).

At the daily productivity cast, samples were taken for measuring primary production and calcification from the 30L Niskin samples (with Silicone O-rings). Water was sampled from 6 light depths: 38.6%, 21.1%, 11.7%, 3.5%, 1.9% and 0.3%. Estimation of those light depths was performed based on the percent light as measured by the scalar PAR sensor aboard the CTD, scaled to the above-water downwelling PAR irradiance measured from the superstructure of USCGC Healy. Given that standard depths were typically sampled (surface, 10m, 25m, 50m, 100m plus the chlorophyll fluorescence maximum), the percent of surface PAR was estimated at each standard depth, then the closest Niskin bottle to each target light depth was chosen for productivity incubation. Often, the water column was only 30-40m and the euphotic depth was shallower still. It was common that water from a single Niskin bottle would be used for more than one simulated in situ incubation sample since the
depth range sampled by the Niskin bottle encompassed several standard light depths. Water samples for incubation were transferred from Niskin bottles to incubation bottles inside the ship’s enclosed hanger. Water samples for $^{14}$C carbon fixation measurements were pre-filtered through 200 $\mu$m nitex mesh to remove large grazers. Incubations were performed in 70 mL polystyrene tissue culture bottles that were previously thoroughly cleaned with 10% HCl, then ethanol, 4 rinses with ship’s distilled water and finally 3 rinses of polished reverse-osmosis water, then rinsed three times with each sea water sample prior to filling. Photosynthesis and calcification were measured using the microdiffusion technique (Paasche and Brubak, 1994) with modifications by Balch et al. (2000) (see also Fabry (2010)). $^{14}$C-bicarbonate (60-100 $\mu$Ci) was added to each water sample. Incubations were performed in triplicate (with an additional sample killed with 2% formalin final concentration). Incubations were performed in simulated in situ conditions on-deck, corrected for both light quantity (using bags made of neutral-density shade cloth) and quality (spectral narrowing using layers of blue acetate as bag inserts). Bottle transfers between the CTD hanger and radioisotope van were always done in a darkened thermal cooler to reduce light and temperature shock to the phytoplankton. Deck incubators consisted of a white plastic tub open to ambient sky light, chilled using surface seawater from the ship’s flowing sea water system. The daily PAR was measured using the ship’s PAR sensor set on top of the ship’s meteorological mast. All filtrations were performed using 0.4 $\mu$m pore-size polycarbonate filters. Following the microdiffusion step, filters and sample “boats” were placed in scintillation vials with 7mL of Ecolume scintillation cocktail. Samples were counted using a Beckman-Coulter LS6500 scintillation counter with channel windows set for $^{14}$C counting with calibration checked with a sealed $^{14}$C standard. Counts were performed for sufficient time to reach 2% precision or 20 minutes for samples with lower counts. Blank $^{14}$C counts were always run for scintillation cocktail as well as the phenethylamine CO$_2$ absorbent.
Standard equations were used for calculating primary production and calcification from the $^{14}$C counts with a 5% isotope discrimination factor assumed for the physiological fixation of $^{14}$C-HCO$_3^-$ (as opposed to $^{12}$C-HCO$_3^-$). Aerial integrations of carbon fixation to the base of the euphotic zone were based on the PAR attenuation measured during the CTD cast and depth integrations were performed using trapezoidal integration. Photosynthesis and calcification measurements were normalized to fluorometer-derived chlorophyll concentration. Samples for chlorophyll analysis were filtered on 25mm, GF/F filters (Whatman) then submerged in 5mL of 90% acetone, extracted for ~ 24h at 3°C. Following centrifugation, the fluorescence of the supernatant was analyzed using a Turner 10-AU fluorometer (Turner Designs, Inc.), previously calibrated with chlorophyll standard (Sigma) (Holm-Hansen et al., 1965).

Intrinsic, carbon-specific growth rates for POC ($\mu_{\text{POC}}$) and PIC ($\mu_{\text{PIC}}$) (units d$^{-1}$) were estimated by dividing the rates of photosynthesis or calcification (in units of moles m$^{-3}$ d$^{-1}$) by POC or PIC concentrations (moles m$^{-3}$), respectively.

3 Results

3.1 Cruise details and hydrographic observations

The general study area of Healy cruise 1101 was the western Arctic (Fig. 1A). The period that the Healy 1101 cruise was in the vicinity of the under-ice algal bloom was between calendar days 183-205. During this period, the southern extent of the ice edge receded north ~100km (Fig. 1B). Water temperatures over the top 5m showed the presence of coldest waters (<-1°C), indicative of Winter Water (Rudels et al., 1990) in the far western portion of the study area, near stations 54-57 (Fig. 1B,C). The next coldest waters were observed in the northern extent of the study area, over the Canadian Basin (Station 100; Fig. 1C). Highest salinities were observed along the southern end of the cruise track, extending (in patches) to station 67 (Fig. 1D), usually associated with waters of 2 to 5°C. Lowest salinities were found in the 0 to -1°C water of the Canada Basin (Fig. 1D).
3.2 Chlorophyll, absorption and fluorescence observations

Chlorophyll concentrations (derived from the continuous underway fluorescence measurements calibrated to discrete chlorophylls) reached greatest values of ~30μg L\(^{-1}\) in the western portion of the study area, where Winter Water reached the top 5m (see white contour line in Fig. 2A). This was the site of the under-ice bloom described earlier (Arrigo et al., 2012). Lowest chlorophyll \(a\) values were seen in the Canadian Basin, (~300X lower at 0.1 μg L\(^{-1}\) (Fig. 2A)). Using a chlorophyll concentration of >2μg L\(^{-1}\) as the criterion for the bloom the largest horizontal dimension measured in the under-ice algal bloom, using the continuous underway system, was ~140km (Fig. 2A).

Particle absorption was also highest in the under-ice algal bloom, with elevated values of ~1m\(^{-1}\), reaching 100km from the ice edge and lowest values in the Canadian Basin (north of station 95; Fig. 2B). Absorption of colored dissolved organic matter (CDOM; \(a_{g412}\)) was elevated within the under-ice bloom and lowest in the Canada Basin (Fig. 2B). Absorption of both CDOM plus detrital matter (\(a_{gp412}\)) was elevated in the under-ice bloom, twice the magnitude of \(a_{g412}\) (Fig. 2C). Values of \(a_{gp412}\) were also elevated near shore (Fig. 2D). The proportion of total absorption at 412 nm contributed by the dissolved (<0.2um) fraction was generally 70-90% over the study area except in the under-ice bloom where only 30-50% of the total absorption was contributed by dissolved materials (Fig. 2F).

Chlorophyll-specific absorption (Fig. 2E) were calculated by first subtracting dissolved absorption from the total particulate and dissolved absorption at all wavelengths, in order to estimate particulate absorption. The particulate absorption was then calculated at each wavelength, subtracting the residual absorption at 715nm to correct for scattering effects (Bricaud et al., 1988). The absorption cross section of chlorophyll at 440nm (\(a^*_{p440}\)) was calculated by dividing the particulate absorption (m\(^{-1}\)) by the chlorophyll concentration (units mg m\(^{-3}\)). Average values of \(a^*_{p440}\) were 0.025 m\(^{2}\) (mg Chl\(^{-1}\)) in the western Winter Water as
well as in the cold waters of the Canadian Basin (Fig. 2E). Highest absorption cross-sections were seen in the warmest, high salinity waters near the Alaskan coast.

Both $a_{p440}$ and $a_{p412}$ were well correlated to chlorophyll biomass. The plot of particulate absorption at 440nm ($a_{p440}$) versus chlorophyll concentration (Fig. 3A) had a Y intercept of 0.002 m$^{-1}$, barely above zero (Table 1), indicating that particulate absorption of phytoplankton was virtually all associated with viable, chlorophyll-containing phytoplankton, not detritus. Further, $a_{p412}$ (which would normally be expected to be representative of particulate detritus) was highly correlated to chlorophyll with a slope of 0.025 m$^2$ (mg Chl)$^{-1}$ and Y intercept of 0.005 m$^{-1}$ (Fig. 3B; Table 1). The high correlation between $a_{p412}$ and $a_{p440}$ can be seen in Fig. 3C, with an $r^2 = 0.975$ and slope of 0.926 (Table 1). Thus, $a_{p412}$ was as good proxy of chlorophyll $a$ as $a_{p440}$, not detritus. Values of dissolved absorption at 412nm ($a_{g412}$) had a positive but far reduced correlation with chlorophyll $a$, however, with only a factor of two increase in $a_{g412}$ observed over >2 orders of magnitude of chlorophyll (Fig. 3D). The relation was still statistically-significant (Table 1).

The slope of the absorption spectrum of dissolved material between 412 and 440 nm (Fig. 4A), $S_g$ (nm$^{-1}$), was calculated according to Stedmon and Markager (2001) as:

$$S_g = ((\ln(a_{g412}/a_{g440}))/440-412)$$

A comparable slope for the detrital and particulate absorption, $S_{pg}$ (nm$^{-1}$), was also calculated by substituting $a_{pg412}$ and $a_{pg440}$ in place of $a_{g412}$ and $a_{g440}$, respectively, in the above equation (Fig. 4B). Note that positive values for these slopes indicate that 412nm absorption >440nm absorption and negative slopes indicate 412nm absorption <440nm absorption. The results show strikingly similar patterns of $S_g$ and $S_{pg}$, with positive values near shore and in the under-ice bloom and negative values in the Canada Basin.

CDOM fluorescence (FDOM) was most elevated in the coldest water of the under-ice algal bloom and over Hannah Shoals. Lowest values were observed near the coast of Alaska.
and in the Canada Basin (Fig. 4C). The relative fluorescent yield of the combined dissolved/detrital material was calculated as the FDOM (from raw, unfiltered seawater) divided by the $a_{g412}$. The term “relative” is used here because FDOM excitation wavelength (370nm) did not match the absorption wavelength measured by the ac-9 (412nm).

The lowest relative FDOM fluorescent yield was observed in the under-ice algal bloom while highest values were observed in the Canada Basin region. Relatively low values were also seen near the coastline of Alaska (Fig. 4D). Highest concentrations of FDOM were in the under-ice bloom, (likely produced by the intense phytoplankton growth) but this FDOM had low relative fluorescent yields (Fig. 4D). The nature of this FDOM can be evaluated through its relation to other bio-optical variables. For example, FDOM was significantly correlated with CDOM (as $a_{g412}$) but the dynamic range in FDOM was less than a factor of 2 over a 10X variation in $a_{g412}$ (and the squared coefficient of correlation was only ~0.3; Fig. 5A). FDOM was better correlated to the chlorophyll $a$ concentration than $a_{g412}$ (Fig. 5B). The best-fit power function to those results accounted for almost 60% of the variance (Table 1). The relative FDOM fluorescence yield also was inversely correlated with the chlorophyll concentration (Fig. 5C) such that the under-ice bloom showed the lowest fluorescent yields, accounting for about 25% of the variance. However, relative FDOM fluorescence yield was strongly inversely correlated to $S_g$ (Fig. 5D) suggesting that the most weakly-colored CDOM and detritus (low $S_g$) had the highest relative fluorescent yield. Note, negative $S_g$ values as shown in Fig. 5D indicate that $a_{gp412}>a_{gp440}$ (which only occurred in the clearest, most oligotrophic waters with extremely low chlorophyll and low suspended particulate matter, such as in the Canada Basin).

3.3 Optical scattering measurements

Optical scattering properties were elevated in the under-ice algal bloom. For example, the acid-labile backscattering-- that backscattering associated with suspended
calcium carbonate-- while generally low, had the most elevated values in the under-ice algal bloom (Fig. 6A). Total particulate backscattering (Fig. 6B) was also elevated within the under-ice algal bloom, such that $b_b'$ only represented, at most, 10% of the total particulate backscattering (Fig. 6C). Total scattering in the under-ice algal bloom reached values as high as $2\text{m}^{-1}$ with an order of magnitude decrease in the Canada Basin (Fig. 6D). Backscattering probability ($b^\sim_p = b_{bp}/b_p$, indicative of all minerogenic scattering, but not just for calcium carbonate) had values of 1% in the under-ice bloom and values up to 3-4% in the Canada Basin and in the open, warm waters south of the ice margin. Low values were seen in the southeastern portion of the study area (Fig. 6E). Waters with highest particle scattering (Fig. 6D) also had highest particle beam attenuation (Fig. 6F). Indeed, particle backscattering, particle scattering and particulate attenuation all showed similar patterns (compare relative patterns in Figs. 6B, D and F).

3.4 Chemical and biogeochemical observations

Vertical sections of PIC, POC and BSi through the under-ice algal bloom all were elevated in regions where the Winter Water reached closest to the surface (Fig. 7). PIC showed elevated values just above the sediments at about 50m, near the shelf break at the most northwesterly position of the cruise, as well as in the region close to the coast of Alaska. Ice-free waters away from the ice edge had low PIC concentrations and elevated POC and BSi. The most elevated PIC in surface waters was seen in the shallowest part of the sections, in ice-free waters, for both legs shown in the section. (Fig. 7A). POC and BSi were highly elevated under the ice, and had a subsurface peak which extended southeast of the ice edge, in the same area where PIC was low (Fig. 7A-C). Deepest waters along the section had lowest values of POC and BSi.

Ratios of PIC:POC were extremely low (~0.25%) in surface waters at the ice edge and within the under-ice algal bloom whereas the ice-free waters over Hannah Shoals (with
elevated PIC; Fig. 7A) had PIC:POC ratios of 1.5-2% (Fig. 8A). Highest PIC:POC ratios were found at 100-150m depth at the shelf break. POC:PON molar ratios of the particulate material in the under-ice algal bloom were elevated above Redfield (10-15) (Fig. 8B). POC:Chl a ratios in the under-ice algal bloom were generally low (50-100 except at the northwest corner of the survey area where there was a region with clearly elevated POC:Chl a ratios (Fig. 8C). Highest POC:Chla ratios in surface waters were found off the NW coast of Alaska.

The nitrate section through the under-ice bloom showed clear evidence of drawdown in the top10-20m as well as evidence of elevated nitrate at the shelf break which was associated with cold Winter Water (Fig. 9A). Silicate drawdown in surface waters also occurred in the under-ice bloom but concentrations of 30μM silicate were observed at the surface at station 54 (Fig. 9B). Residual nitrate (defined as the nitrate concentration minus the silicate concentration) (Townsend et al., 2010) showed negative values of -20 to -40μM under the ice, emphasizing the strong reduction of nitrate relative to silicate (Fig. 9C).

Primary production and calcification showed highest values within the under-ice bloom. While the primary production rates were high on any standard (~400 mg C m⁻³ d⁻¹; Fig. 9A; Table 2), the calcification rates were only 0.4% of the primary production values (Fig. 10B). Carbon fixation dropped off rapidly in the ice free waters, as well. Primary production and calcification both attenuated with depth. Integrated primary productivity rates in the bloom approached 3g m⁻² d⁻¹ whereas integrated calcification was ~10 mg m⁻² d⁻¹ (Table 2). The C:P ratio in the bloom averaged 0.33% over the water column. Chlorophyll-normalized primary production was 5 gC (g Chl)⁻¹ d⁻¹ (Table 2). Integrated calcification normalized by integrated chlorophyll was also low, 0.02 gC (g Chl)⁻¹ d⁻¹ (Table 2). Intrinsic, carbon-specific growth rates for POC (μₚₒᶜ) approached 0.4 d⁻¹ (Fig. 10C) while μₚᵢᶜ
approached 1d⁻¹ (Fig. 10D). Integrated chlorophyll biomass in the center of the under-ice bloom was 490 mg m⁻² (Table 2).

3.5 Microscopy

Scanning electron microscopy results from the under-ice algal bloom showed strong dominance by diatoms, with *Chaetoceros* sp, *Fragilariopsis* sp. and *Thallasiosira* sp. (Fig. 11A-F). Coccoliths of the coccolithophore, *Emiliania huxleyi* were also observed. While the coccoliths were >4um in diameter (which typically is a trait more characteristic of the type B morphotype) (Poulton *et al.*, 2011), there were traits that align with Type A morphotypes--the distal shield was larger than the proximal shield, the radial elements were robust, and the elements in the central area were curved (Fig. 11G, H) (Poulton *et al.*, 2011).

4 Discussion

4.1 Size of bloom based on continuous underway measurements

The hydrographic measurements made by our surface underway system clearly showed the coolest waters (-1.6°C under the ice with salinities of 30-31), characteristic of Arctic Winter Water (Coachman and Aagaard, 1974; Coachman and Barnes, 1961; Rudels *et al.*, 1990; Rudels *et al.*, 2004). Based on the continuous surface hydrographic data, the maximum horizontal length-scale of the Winter Water mass was about 150km (Fig. 1), close to the length of the elevated chlorophyll concentration for the bloom (~140km; Fig. 2A).

4.2 Interpreting the absorption properties of the under-ice algal bloom

The particulate absorption at 440nm showed similar trends to the chlorophyll concentration, as expected (Fig. 2B), however, the chlorophyll specific absorption at 440nm (the absorption cross section, \(a_{\text{p440}}\)) averaged 0.027(SE = ±9.6x10⁻⁵) m² (mg Chl)⁻¹ over the study region (Figs. 2E; 10A), well within the range observed for phytoplankton (Bricaud *et al.*, 1983), in particular diatoms (Bricaud *et al.*, 1988; Sathyendranath *et al.*, 1987). Such variability is known to be a function of pigment composition, cell size and internal
chlorophyll concentration. The predominance of low values of the absorption cross section ($a_p^{*440}$; Fig. 2E) suggest that the pigments were highly packaged, characteristic of large diatoms. However, the $a_p^{*440}$ values observed near the coast (0.10-0.23 m$^2$ (mg Chl)$^{-1}$) were far higher than expected for phytoplankton and these may have resulted from other sources of absorbing particulate matter, or the presence of photoprotective pigments. It should be noted that the two cruise legs with such high $a_p^{*440}$, southeast of Hanna Shoals were performed at the end of the cruise (calendar day 204-205; July 23-24), almost one month after the earlier section through the under-ice bloom, and water temperatures had warmed 3.5-4°C and light levels would have been higher, making phytoplankton cells more high-light-adapted.

The shape of the particulate absorption spectrum contains information on phytoplankton size. Ciotti et al. (2002) normalized the spectral absorption at a given wavelength, $\lambda$ ($a_{ph(\lambda)}$; m$^{-1}$), by the mean absorption across the visible spectrum ($<a_{ph}>$) and demonstrated that, for 440nm light, the closer the value of $a_{ph(440)}/<a_{ph}>$ to 1.5, the greater the proportion of microplankton in the sample and alternatively, the closer the value to 3, the larger proportion of smaller phytoplankton. Using this technique, they were able to discriminate between picophytoplankton (<0.2 $\mu$m), ultraphytoplankton (2-5 $\mu$m), nanophytoplankton (5-20 $\mu$m) and microphytoplankton (>20 $\mu$m). Moreover, they could model the normalized phytoplankton absorption of any assemblage using combinations of just the micro- and pico-phytoplankton spectra. Ciotti et al. (2002) used the methanol extraction technique (Kishino et al., 1984) to unequivocally measure the spectral absorption of particulate detritus which they then subtracted from the total particulate absorption spectrum to calculate phytoplankton absorption ($a_{ph(\lambda)}$).

Unfortunately, we had no methanol extraction data so we had to use other means to ascertain if $a_p(\lambda)$ approximated $a_{ph}(\lambda)$. In over half of the study area, >95% of absorption at 412nm was from dissolved material, hence absorption by particulate detritus was minimal
Particulate absorption at 412 nm was only significant in the under-ice algal bloom (see Fig. 2F where \(a_g_{412}/a_{pg412}\) was 20-50%) as well as close to the Alaskan coast. However, the carbon:chlorophyll ratio in the bloom was ~50 (Fig. 8C), more representative of actively growing phytoplankton than assemblages dominated by particulate detritus (Geider, 1987). Further, the plots of \(a_{p440}\) and \(a_{p412}\) versus chlorophyll showed that particulate absorption of phytoplankton was virtually all associated with viable, chlorophyll-containing phytoplankton, not detritus (Fig. 3; Table 1). The reduced correlation between chlorophyll \(a\) and \(a_g_{412}\) (Fig. 3D) is consistent with other sources of \(a_g_{412}\) than just phytoplankton, such as terrestrial sources.

In short, while the \(a_{p412}\) was elevated in the bloom, it strongly covaried with chlorophyll, indicative of minimum amounts of particulate detritus. We conclude that detrital absorption at 440 nm was negligible in the bloom such that \(a_p(440)\) would have approximated \(a_{ph}(440)\). This allowed calculation of \(a_{ph(440)}/\langle a_{ph}\rangle\) (Ciotti et al., 2002) along the cruise track (Fig. 12A) as well as the resultant fraction of picoplankton that would have been expected in the assemblages (S_f; Fig. 12B). Values of \(a_{ph(440)}/\langle a_{ph}\rangle\) varied from 1.5-2, suggesting that the entire study area was strongly dominated by microplankton (Ciotti and Bricaud, 2006; Ciotti et al., 2002). This conclusion was entirely consistent with the scanning electron microscopy results, as well (Fig. 11).

### 4.3 CDOM, FDOM and fluorescence yield

These results suggest that under-ice phytoplankton were an important source of FDOM and that FDOM fluorescence accounted for only ~30% of the variance in CDOM. The change in dissolved absorption between 412 and 440 nm, normalized by the change in wavelength, \(S_g\) (Roesler and Perry, 1989) has been suggested to vary as a function of the source of CDOM. Steeper slopes typically are more representative of lignin-rich, terrestrially-derived materials (Stedmon and Markager, 2001). In this study, \(S_g\) values of
0.01 in the bloom were more representative of low-colored, autochthonous, marine CDOM (Carder et al., 1989), as opposed to highly-colored, terrestrially-derived CDOM (Stedmon and Markager, 2001)(Fig. 4A). In the Canada Basin, absorption at 440nm was greater than at 412nm, likely due the extremely low CDOM concentrations there.

The CDOM fluorometer used here had excitation/emission peaks of 370 and 460nm, respectively. These correspond roughly to the red-shifted, “Peak C”, humic-like, CDOM fluorophore originally described by Coble (1996). FDOM can be produced by a variety of different compounds, and the fluorescence yields can be affected by a multitude of physical and chemical factors (including pH, temperature, hydrogen bonding, metal binding, etc.). Biology is also involved since bacteria (Rochelle-Newall and Fisher, 2002) and phytoplankton (Romera-Castillo et al., 2010) are both sources of FDOM. Our results showed no relation of relative fluorescence yield to water temperature (results not show). Moreover, the data support the conclusions of Romera-Castillo et al. (2010) that phytoplankton are producers of FDOM (Fig. 5B). The strong linear relation between relative fluorescent yield and $S_g$ was not expected but shows a highly predictable continuum of relative fluorescence yield across these under-ice waters. With such a strong relationship, these results would suggest an alternative way to predict $S_g$ using FDOM fluorescence yield.

4.4 Significance of bloom magnitude

The levels of productivity found in the under-ice bloom represent some of the highest levels found in nature (Balch et al., 1992; Morel and Maritorena, 2001). Integrated primary production rates in the bloom center ($2.86\text{ g m}^{-2} \text{ d}^{-1}$) were well above under-ice rates observed previously (Gosselin et al., 1997), yet the water column assimilation efficiency of $5.8 \text{ g C (g chl)}^{-1} \text{ d}^{-1}$ was still well below the theoretical maximum for phytoplankton (Falkowski, 1981). In an integrated sense, calcification rates represented only 0.33% of the integrated productivity (Table 2). Similarly, in a pure coccolithophore culture (or dense
c coccolithophore blooms in nature), one would expect a chlorophyll-normalized calcification of \(~1.19 \text{ gPIC fixed (g chl)}^{-1} \text{ h}^{-1}\) (or \(28.6 \text{ gPIC fixed (g chl)}^{-1} \text{ d}^{-1}\))(Balch et al., 2007). The chlorophyll normalized values observed in this study (0.02 gPIC fixed (g chl)^{-1} d^{-1}; Table 2) were three orders of magnitude less than this, simply due to the dominance of diatoms (Table 2).

4.5 Coccolithophores were present in the under-ice algal bloom

Optical scattering, PIC, SEM and calcification results demonstrated the presence of coccolithophores in the under-ice algal bloom but not as a dominant part of the community. Values of acid-labile backscattering, compared to subpolar or subtropical waters, were low, approaching the sensitivity of the technique and certainly indicative of a non-bloom, background population of coccolithophores (Balch et al., 2004; Balch et al., 2011; Balch et al., 2005; Balch et al., 1996). As a percentage of the total backscattering (Fig. 6C; 4-6%) this is lower than the typical percentage of backscattering typically attributed to coccolithophores, even in oligotrophic gyres (Balch et al., 2010). PIC:POC ratios were characterized by low values (<0.2%) in the under-ice bloom, too, again suggestive of low biogeochemical impact of coccolithophores in this under-ice bloom.

In general, the distribution and fixation of PIC mirrored that of POC, and it appeared that coccolithophores were responding in the same manner to increased light penetration through the ice as were the diatoms and other algal groups (Figs. 10). Given the elevated nutrients found the Arctic Winter Water, all groups were released from light limitation together. Barber and Hiscock (2006) described algal communities in which all the phytoplankton groups responded with increased growth rate to enhanced iron, they also observed that the picoplankton response was more muted than that of the diatoms because picoplankton were selectively grazed down by the fast-responding microzooplankton (Landry, 2002). In the case of the under-ice algal bloom, it is possible that enhanced growth
of coccolithophores (by release from light limitation) was also muted by grazing by fast-
responding protistan predators. Indeed, standing stocks of POC and BSi showed high-
covariance under the ice (Fig. 7); both showed a subsurface “tongue” that extended out from
under the ice on the northern part of the under-ice algal bloom while PIC, on the other hand,
was actually reduced in that feature and greatest PIC concentrations were observed almost
100km away from the ice edge, in ice-free water of 3-4°C (Figs. 1 and 5). The appearance of
*E. huxleyi* in waters of the Southern Ocean also occurs at such temperatures (Balch *et al.*
2011; Cubillos *et al.*, 2007; Gravalosa *et al.*, 2008; Holligan *et al.*, 2010; Mohan *et al.*, 2008).
Elevated concentrations of PIC and BSi also were observed just above the sediments near the
shelf break, at 40-60m depth, suggesting that resuspension also may have been important
source of these biogenic mineral particles. This could be seen in the PIC:POC ratios which
were extremely low in the under-ice algal bloom (0-0.2%) but elevated with depth, with
highest values observed in the 100-150m-deep, northwest portion of the under-ice algal
bloom (at 3%; Fig. 8A). As noted above, resuspension may have influenced this ratio at the
shelf break. Alternatively, preferential remineralization of POC over PIC could also have
produced this pattern (Honjo *et al.*, 2008). The saturation states for calcite ($\Omega_{\text{calcite}}$) and
aragonite ($\Omega_{\text{aragonite}}$) showed that waters were saturated for calcite and aragonite in this region
(Bates personal communication), thus dissolution of calcite and aragonite would have been
unlikely.

4.6 *Nutrient limitation and a mismatch in carbon standing stocks versus rates of carbon
fixation*

Molar ratios of C:N were, for the most part, greater than the 6.6 C:N Redfield ratio
(Redfield *et al.*, 1963) in the top 20m of the under-ice feature (Fig. 8B) but given that nitrate
levels under the ice had been depleted to micromolar levels (Fig. 9A), then it would be
expected that the populations would have shown signs of nitrogen limitation. This
interpretation was buttressed by the low POC:Chlorophyll ratios in under-ice algal bloom waters where nitrate depletion had only occurred in the upper 10m of the water column. Indeed, regions of elevated POC:PON corresponded to high POC:Chlorophyll, for example at the northwest corner of the study area. Deeper Winter Water under the ice was rich in nitrate and silicate as evidenced by the covariance of the -1.6 isotherm and isolines of silicate and nitrate (Fig. 9A and B). Moreover, Winter Water was elevated in silicate relative to nitrate (by 40μm at 60m depth; Fig. 9C). In regions where chlorophyll and POC were highest, the residual nitrate was closer to zero, suggesting that the phytoplankton community uniformly drew down nitrate and silicate towards zero. This could have resulted from either adjustments of diatom cell quotas as they consumed the silicate (Baines et al., 2011) or depletion of nitrate by the majority diatom assemblage and minority, non-diatom phytoplankton plus silicate depletion by just the diatoms, in such a way that both were depleted together. What seems clear is that where physical processes brought Winter Water upwards under the ice, the release of the phytoplankton from light limitation by melt ponds then allowed nutrient drawdown to occur such that all algae began to show signs of both nitrogen limitation (increased C:N) and silicate limitation (reduced silicate with increasing BSi).

Overall, the history of the bloom formation caused a mismatch in the standing stocks and rates of fixation of particulate organic and inorganic carbon. Highest carbon fixation (for photosynthesis and calcification) was observed further into the ice, in regions where the standing stocks of POC and chlorophyll were not the highest. Elevated standing stocks of PIC and POC were found in waters where nutrients had already been depleted whereas highest productivity rates were seen where nutrients had not yet been depleted.
4.7 Conclusion- Under-ice coccolithophores and global change

The aforementioned observations demonstrate that coccolithophores were present in the under-ice algal bloom but that their relative contribution to carbon cycling was minor compared to the carbon fixation by the diatom-dominated assemblages. Coccolithophore presence was observed analytically (ICP-OES), optically and microscopically. The low numbers of coccolithophores in the under-ice bloom is consistent with previous observations of algal communities in ice-covered waters.

A comparison of the calcification rates in the under-ice algal bloom of ICESCAPE with those rates measured on polar coccolithophores by Charalampopoulou et al. is informative. Highest total calcification rates at their ice edge station was ~0.6 mg C m\(^{-3}\) d\(^{-1}\) at 20m depth, some 40% of what we observed for the under-ice algal bloom (1.5 mg C m\(^{-3}\) d\(^{-1}\)). Charalampopoulou et al. (2011) also measured calcification in the marginal ice zone and a Svalbard fjord and found calcification rates 20-75 times lower than the calcification rates in Chukchi Sea under-ice algal bloom (0.02-0.07 mg C m\(^{-3}\) d\(^{-1}\)).

This data set also provides the opportunity to compare the growth rates of the phytoplankton (\(\mu_{\text{POC}}\) in Fig. 10C, clearly dominated by diatoms) to rates predicted in the classic treatise by Epply (1972) on the effects of temperature and phytoplankton growth. Using his equation 1 (or 1a), the predicted maximal growth rate of phytoplankton in Winter Water of -1.6°C would have been 0.77 doublings d\(^{-1}\) (= 1.11 d\(^{-1}\) specific growth rate). The highest POC-specific growth rates that we observed (~0.35 d\(^{-1}\)) were ~30% of the maximum growth rate predicted by the Eppley (1972) equation, possibly reflecting the effect of the previous nitrate draw-down in the surface waters. Moreover, if the intrinsic rates of increase of PIC were coupled to coccolithophore growth rates, as shown previously (Fritz and Balch, 1996), then the observed PIC-specific growth rates (0.9 d\(^{-1}\)) would have been much closer to
the maximal growth rates predicted by Eppley (1972). This would have been expected anyhow given the well-known observations that coccolithophores such as *E. huxleyi* can maintain higher growth rates at lower nitrate concentrations than, for example, diatoms, due to their significantly lower half saturation constants for nitrate uptake (Eppley *et al.*, 1969; Margalef, 1978).

The hypothesis central to the formation of the under-ice algal bloom is that melt ponds on top of the ice allowed light to penetrate the meter-thick ice, thus releasing under-ice algae from severe light limitation (Arrigo *et al.*, 2012). One can then ask how long it would have taken for phytoplankton with chlorophyll concentrations below the limit of detection to grow to the levels seen in the under-ice bloom. This also provides insights whether the bloom could have formed in place or was somehow advected and concentrated there. Assuming a background concentration of chlorophyll of 0.01 mg m\(^{-3}\) prior to the bloom (0.04 mg m\(^{-3}\) is typically used as the limit of detection for the fluorometric chlorophyll technique using standard practices and volumes (Parsons *et al.*, 1984)), then using the logistic growth equation, and the above \(\mu_{POC}\) of 0.35 d\(^{-1}\), then it would have taken \(\approx 23\) d to reach a chlorophyll concentration of 30 mg m\(^{-3}\) (i.e. time (days) = \(\ln[30/0.01]/0.35\), assuming no grazing or other loss terms. Thus, for the above hypothesis to be consistent with our observations, than the melt ponds would have had to be present for at least three weeks prior to our measurements for there to be sufficient time for the high chlorophyll levels to form. Moreover, it is assumed that once nitrogen became limiting, then the diatom growth would have slowed (alternatively, grazing might have also reduced the net growth below maximal growth rates).

This same calculation can be done for PIC, however, in this case, the estimated intrinsic calcification rate, \(\mu_{PIC}\), was greater (0.9 d\(^{-1}\); Fig. 10). Even beginning with just 10 *E. huxleyi* cells L\(^{-1}\) (each containing 15 coccoliths of 0.2 pg PIC (Balch, 1991; Balch *et al.*, 1991))
(or 0.25pmoles PIC/cell) for a total of 2.5pmoles PIC L⁻¹), then after 23d, the water would have contained several mmoles PIC L⁻¹. Such was not the case, however, with PIC levels only 0.15 μmols L⁻¹ in surface waters of the under-ice algal bloom (Fig. 7), thus suggesting other forces were acting on the coccoliths (sinking, grazing and/or dissolution) to keep concentrations low, or simply that such PIC-specific growth rates of coccolithophores were not sustained for 23d (most likely).

The under-ice bloom observations first described by Arrigo et al. (2012) were unique regarding the spatial scale and magnitude of such blooms that could exist under 1 meter-thick ice. Results presented here represent the first observations showing the presence of low, but measurable, numbers of coccolithophores, >100km into the thick polar ice cap in a massive under-ice feature. Remote sensing results of Smythe (2004) suggest that large scale coccolithophore blooms are becoming more abundant in ice-free polar waters. What has been missing is whether there are populations far into the ice sheet, capable of growth given the proper conditions of nutrients and light. Our results unequivocally show that there is a resident population of coccolithophores such as *E. huxleyi* that are poised to grow and calcify given their release from light limitation as melt ponds form and the polar ice cap melts.

Given intrinsic calcification rates, it is not known why there are not more coccoliths present in these waters. It has been shown that pH has a strong influence on coccolithophores in polar waters (Charalampopoulou *et al.*, 2011). Ocean acidification will cause the largest decline in carbonate saturation states in high latitude, polar waters (Feely *et al.*, 2009), especially after the polar ice cap melts, allowing more efficient air-sea gas equilibration. A key point, however, will be the balance that warming/release from light limitation will play in encouraging coccolithophore growth in Arctic waters versus the inhibitory role that increasing ocean acidification will have on coccolithophore production and growth in polar waters, in the face of climate change.
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References

Arrigo, K.R., Perovich, D.K., Pickart, R.S., Brown, Z.W., van Dijken, G.L., Lowry, K.E., Mills, M.M., Palmer, M.A., Balch, W.M., Bahr, F.L., Bates, N.R., Benitez-Nelson, C., Bowler, B., Brownlee, E., Ehn, J.K., Frey, K.E., Garley, R., Laney, S.R., Lubelczyk, L., Mathis, J.T., Matsuoka, A., Mitchell, B.G., Moore, G.W.K., Ortega-Retuerta, E., Pal, S., Polashenski, C.M., Reynolds, R.A., Scheiber, B., Sosik, H.M., Stephens, M., Swift, J.H., 2012. Massive phytoplankton blooms under Arctic sea ice. Science 336 (6087), 1408-1409.

Arrigo, K.R., van Dijken, G., Pabi, S., 2008. Impact of a shrinking Arctic ice cover on marine primary production. Geophysical Research Letters 35 (19).

Baines, S.B., Twining, B.S., Vogt, S., Balch, W.M., Fisher, N.S., Nelson, D.M., 2011. Elemental composition of equatorial Pacific diatoms exposed to additions of silicic acid and iron. Deep-Sea Research II 58, 512–523.

Balch, W., 1991. Erratum from "Biological and optical properties of mesoscale coccolithophore blooms in the Gulf of Maine" by Balch, W. M., P. M. Holligan, S. G. Ackleson and K. J. Voss. Limnology and Oceanography 36 (7), 1462.

Balch, W.M., Bowler, B.C., Drapeau, D.T., Poulton, A., Holligan, P., 2010. Biominerals and the vertical flux of particulate organic carbon from the surface ocean. Geochemical Research Letters 37 (L22605), 1-6.

Balch, W.M., Drapeau, D., Fritz, J., 2000. Monsoonal forcing of calcification in the Arabian Sea. Deep-Sea Research II 47, 1301-1337.

Balch, W.M., Drapeau, D.T., Bowler, B.C., Booth, E., 2007. Prediction of pelagic calcification rates using satellite-measurements. Deep -Sea Research II (Chapman Calcification Conference Special Volume) 54, 478-495.
Balch, W.M., Drapeau, D.T., Bowler, B.C., Booth, E.S., Goes, J.I., Ashe, A., Frye, J.M., 2004. A multi-year record of hydrographic and bio-optical properties in the Gulf of Maine: I. Spatial and temporal variability. Progress in Oceanography 63, 57-98.

Balch, W.M., Drapeau, D.T., Bowler, B.C., Booth, E.S., Lyczskowski, E., Alley, D., 2011. The contribution of coccolithophores to the optical and inorganic carbon budgets during the Southern Ocean Gas Experiment: New evidence in support of the "Great Calcite Belt" hypothesis. Journal of Geophysical Research- Special Issue 116, 1-14.

Balch, W.M., Drapeau, D.T., Bowler, B.C., Booth, E.S., Windecker, L.A., Ashe, A., 2008. Space-time variability of carbon standing stocks and fixation rates in the Gulf of Maine, along the GNATS transect between Portland, ME and Yarmouth, NS. Journal of Plankton Research 30 (2), 119-139.

Balch, W.M., Evans, R., Brown, J., Feldman, G., McClain, C., Esais, W., 1992. The remote sensing of ocean primary productivity-use of a new data compilation to test satellite algorithms. Journal of Geophysical Research 97, 2279-2293.

Balch, W.M., Gordon, H.R., Bowler, B.C., Drapeau, D.T., Booth, E.S., 2005. Calcium carbonate budgets in the surface global ocean based on MODIS data. Journal of Geophysical Research Oceans 110 (C7), C07001, doi:07010.01029/02004JC002560.

Balch, W.M., Holligan, P.M., Ackleson, S.G., Voss, K.J., 1991. Biological and optical properties of mesoscale coccolithophore blooms in the Gulf of Maine. Limnology and Oceanography 36, 629-643.

Balch, W.M., Kilpatrick, K., Holligan, P.M., Harbour, D., Fernandez, E., 1996. The 1991 coccolithophore bloom in the central north Atlantic. II. Relating optics to coccolith concentration. Limnology and Oceanography 41, 1684-1696.
Barber, R.T., Hiscock, M.R., 2006. A rising tide lifts all phytoplankton: Growth response of other phytoplankton taxa in diatom-dominated blooms. Global Biogeochemical Cycles [Global Biogeochem. Cycles]. 20 (4).

Braarud, T., 1935. The “Øst” expedition to the Denmark Strait. II. The phytoplankton and its conditions of growth (including some qualitative data from the Arctic in 1939). Hvalra’d. Skr. 10, 173.

Bricaud, A., Bédhomme, A.-L., Morel, A., 1988. Optical properties of diverse phytoplanktonic species: experimental results and theoretical interpretation. Journal of Plankton Research 10 (5), 851-873.

Bricaud, A., Morel, A., Prieur, L., 1983. Optical efficiency factors of some phytoplankters. Limnology and Oceanography 28, 816-832.

Brzezinski, M.A., Nelson, D.M., 1989. Seasonal changes in the silicon cycle within a Gulf Stream warm-core ring. Deep-Sea Research 136, 1009-1030.

Bursa, A.S., 1961. The annual oceanographic cycle at Igloolik in the Canadian Arctic II. The phytoplankton. J. Fish. Res. Bd. Can. 18, 563-615.

Carder, K.L., Steward, R.G., Harvey, G.R., Ortner, P.B., 1989. Marine humic and fluvic acids: Their effects on remote sensing of ocean chlorophyll. Limnology and Oceanography 34, 68-81.

Charalampopoulou, A., Poulton, A.J., Tyrrell, T., Lucas, M.I., 2011. Irradiance and pH affect coccolithophore community composition on a transect between the North Sea and the Arctic Ocean. Marine Ecology Progress Series 431, 25-43.

Ciotti, A., Bricaud, A., 2006. Retrievals of a size parameter for phytoplankton and spectral light absorption by colored detrital matter from water-leaving radiances at SeaWiFS channels in a continental shelf region off Brazil. Limnology and Oceanography: Methods 4, 237-253.
Ciotti, A.M., Lewis, M.R., Cullen, J.J., 2002. Assessment of the relationships between dominant cell size in natural phytoplankton communities and the spectral shape of the absorption coefficient. Limnology and Oceanography 47 (2), 404-417.

Coachman, L.K., Aagaard, K., 1974. Physical oceanography of the Arctic and subarctic seas. In: Herman, Y. (Ed.), Marine geology and oceanography of the Arctic seas. Springer Verlag, New York, pp. 1-72.

Coachman, L.K., Barnes, C.A., 1961. The contribution of Bering Sea water to the Arctic Ocean. Arctic 14, 147–161.

Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry 51, 325-346.

Codispoti, L.A., Kelly, V., Thessen, A., Matrai, P., Suttles, S., Hill, V., Steele, M., Light, B., 2012. Synthesis of primary production in the Arctic Ocean: III. Nitrate and phosphate based estimates of net community production. Progress in Oceanography 110, 126-150.

Cubillos, J.C., Wright, S.W., Nash, G., De Salas, M.F., Griffiths, B., Tilbrook, B., Poisson, A., Hallegraeff, G.M., 2007. Calcification morphotypes of the coccolithophorid Emiliania huxleyi in the Southern Ocean: Changes in 2001 to 2006 compared to historical data. Marine Ecology Progress Series 348, 47-54.

Ehrenberg, C.G., 1841. Einen Nachtrag zu dem Vortrage über Verbreitung und Einfluß des mikroskopischen Lebens in Süd- und Nord-Amerika. D. Akad. Wiss., Berlin, Monatsber., 202-207.

Eppley, R.W., 1972. Temperature and phytoplankton growth in the sea. Fishery Bulletin 70, 1063-1085.

Eppley, R.W., Peterson, B., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. Nature 282, 677-680.
Eppley, R.W., Rogers, J.N., McCarthy, J.J., 1969. Half-saturation constants for uptake of nitrate and ammonium by marine phytoplankton. Limnology and Oceanography 14 (6), 912-920.

Fabry, V.J., Balch, W.M., 2010. Direct measurements of calcification rates in planktonic organisms. In: Riebesell, U., Fabry, V.J., Hansson, L., Gattuso, J.-P. (Eds.), Guide to Best Practices in Ocean Acidification Research and Data Reporting. European Project on Ocean Acidification (EPOCA), Bremerhaven, Germany, pp. 185-196.

Falkowski, P., 1981. Light-shade adaptation and assimilation numbers. Journal of Plankton Research 3, 203-217.

Feely, R., Doney, S.C., Cooley, S.R., 2009. Ocean acidification: present conditions and future changes in a high-CO₂ world. Oceanography 22 (4), 36-47.

Fritz, J.J., Balch, W.M., 1996. A coccolith detachment rate determined from chemostat cultures of the coccolithophore *Emiliania huxleyi*. Journal of Experimental Marine Biology and Ecology 207, 127-147.

Geider, R.J., 1987. Light and temperature dependence of the carbon to chlorophyll a ratio in microalgae and cyanobacteria: Implications for physiology and growth of phytoplankton. New Phytologist 106, 1-34.

Goldstein, J., Newbury, D., Joy, D., Lyman, C., Echlin, P., Lifshin, E., Sawyer, L., Michael, J., 2003. Scanning electron microscopy and X-ray microanalysis. Springer Science + Business Media, LLC, New York.

Gosselin, M., Levasseur, M., Wheeler, P.A., Horner, R.A., Booth, B.C., 1997. New measurements of phytoplankton and ice algal production in the Arctic Ocean. Deep Sea Research II 44 (8), 1623–1644.

Gravalosa, J.M., Flores, J.-A., Sierro, F.J., Gersonde, R., 2008. Sea surface distribution of coccolithophores in the eastern Pacific sector of the Southern Ocean (Bellingshausen
and Amundsen Seas) during the late austral summer of 2001. Marine Micropaleontology 69 (1), 16-25.

Haidar, A.T., Thierstein, H.R., 2001. Coccolithophore dynamics off Bermuda (N. Atlantic). Deep Sea Research 48 (8-9), 1925-1956.

Hewes, C.D., Holm-Hansen, O., 1983. A method for recovering nanoplankton from filters for identification with the microscope: The filter-transfer-freeze (FTF) technique. Limnology and Oceanography 28, 389-394.

Hill, V.J., Matrai, P.A., Olson, E., Sutlles, S., Steele, M., Codispoti, L.A., Zimmerman, R.C., 2013. Synthesis of integrated primary production in the Arctic Ocean: II. In situ and remotely sensed estimates. Progress in Oceanography 110, 107-125.

Holligan, P.M., Charalampospolou, A., Hutson, R., 2010. Seasonal distributions of the coccolithophore, Emiliania huxleyi, and of particulate inorganic carbon in surface waters of the Scotia Sea. Journal of Marine Systems 82 (4), 195-205.

Holm-Hansen, O., Lorenzen, C.J., Holmes, R.W., Strickland, J.D.H., 1965. Fluorometric determination of chlorophyll. J. Cons Perm. Int. Explor. Mer. 30, 3-15.

Honjo, S., Manganini, S.J., Krishfield, R.A., Francois, R., 2008. Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983. Progress in Oceanography 76 (3), 217-285.

Horner, R., 1984. Phytoplankton abundance, chlorophyll a, and primary production in the western Beaufort Sea. In: Barnes, P., Schell, D.M. (Eds.), The Alaskan Beaufort Sea: Ecosystems and environments. Academic Press, Inc., pp. 205-309.

JGOFS, 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements. In: Knap, A. (Ed.), Report no. 19 of the Joint Global Ocean Flux Study. Scientific committee on oceanic research, international council of scientific unions. Intergovernmental Oceanographic Commission, Bergen, Norway, p. 170.
Kishino, M., Booth, C.R., Okami, N., 1984. Underwater radiant energy absorbed by phytoplankton, detritus, dissolved organic matter, and pure water. Limnology and Oceanography 29 (2), 340-349.

Landry, M.R., 2002. Integrating classical and microbial food web concepts: Evolving views from the open-ocean tropical Pacific. Hydrobiologia 480, 29–39.

Manton, I., Sutherland, J., McCully, M., 1976a. Fine-structural observations on coccolithophorids from South Alaska in the genera Papposphaera Tangen and Pappomonas Manton and Oates. British Phycological Journal 11, 225–238.

Manton, I., Sutherland, J., Oates, K., 1976b. Arctic coccolithophorids: two species of Turrisphaera gen. nov. from West Greenland, Alaska and the North-West Passag. Proceedings of the Royal Society, Series B. 194, 179-194.

Manton, I., Sutherland, J., Oates, K., 1977. Arctic coccolithophorids: Wigwamma arctica gen. et sp. nov. from Greenland and Arctic Canada, W. annulifera sp. nov. from South Africa and south Alaska and Calciarcus alaskensis gen. et sp. nov. from S. Alaska. Proceedings of the royal Society Ser. B 197, 145-168.

Margalef, R., 1978. Life-forms of phytoplankton as survival alternatives in an unstable environment. Oceanologica Acta 1 (4), 493-509.

Matrai, P., Codispoti, L., Hill, V., Light, B., Steele, M., 2013. Synthesis of annual primary production in the Arctic Ocean. Progress in Oceanography 110, 93-106.

McIntyre, A., Be, A.W.H., 1967. Modern coccolithophoridea of the Atlantic Ocean. I. Placoliths and cyrtoliths. Deep Sea Res. 14, 561-597.

Mobley, C.D., 1994. Light and water: Radiative transfer in natural waters. Academic Press, New York.
Mohan, R., Mergulhao, L.P., Guptha, M.V.S., Rajakumar, A., Thamban, M., Anikumar, N., Sudhakar, M., Ravindra, R., 2008. Ecology of coccolithophores in the Indian sector of the Southern Ocean. Marine Micropaleontology 67, 30-45.

Morel, A., Maritorena, S., 2001. Bio-optical properties of oceanic waters: A reappraisal. Journal of Geophysical Research 106 (C4), 7163-.

Okada, H., Honjo, S., 1973. Distribution of coccolithophorids in the north and equatorial pacific ocean: Quantitative data on samples collected during leg 30, OSHORO MARU, 1968 and LEG HK69-4, HAKUHO MARU, 1969. Woods Hole Oceanographic Institution, Woods Hole, pp. 1-58.

Paasche, E., Brubak, S., 1994. Enhanced calcification in the coccolithophorid Emiliania huxleyi (Haptophyceae) under phosphorus limitation. Phycologia 33, 324-330.

Parsons, T.R., Maita, Y., Lalli, C.M., 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press Inc., New York.

Poulin, M., Daugbjerg, N., Gradinger, R., Ilyash, L., Ratkova, T., von Quillfeldt, C., 2011. The pan-Arctic biodiversity of marine pelagic and sea-ice unicellular eukaryotes: a first-attempt assessment. Marine Biodiversity 41, 13-28.

Poulton, A.J., Sanders, R., Holligan, P.M., Adey, T., Stinchcombe, M., Brown, L., Chamberlain, K., 2006. Phytoplankton mineralisation in the tropical and subtropical Atlantic Ocean. Global Biogeochemical Cycles 20 (4), GB4002, doi:10.1029/2006GB002712.

Poulton, A.J., Young, J.R., Bates, N.R., Balch, W.M., 2011. Biometry of detached Emiliania huxleyi coccoliths along the Patagonian Shelf. Marine Ecology Progress Series 443, 1-17.
Raitsos, D.E., Lavender, S.J., Pradhan, Y., Tyrrell, T., Reid, P.C., Edwards, M., 2006. Coccolithophore bloom size variation in response to the regional environment of the subarctic North Atlantic. Limnology and Oceanography 51 (5), 2122-2130.

Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of sea-water. In: Hill, M.N. (Ed.), The Sea. Wiley, New York, pp. 26-77.

Rochelle-Newall, E., Fisher, T.R., 2002. An investigation into phytoplankton as a source of chromophoric dissolved organic matter. Marine Chemistry 77, 7-21.

Roesler, C.S., Perry, M.J., 1989. Modeling in situ phytoplankton absorption from total absorption spectra in productive inland marine waters. Limnology and Oceanography 34 (8), 1510-1523.

Romera-Castillo, C., Sarmento, H., Alvarez-Salgado, X.A., Gasol, J.M., Marrasé, C., 2010. Production of chromophoric dissolved organic matter by marine phytoplankton. Limnology and Oceanography 55 (1), 446–454.

Rudels, B., Larsson, A.-M., Sehlstedt, P., 1990. Stratification and water mass formation in the Arctic Ocean: some implications for the nutrient distribution. In: Sakshaug, E., Hopkins, C.C.E., Oritsland, N.A. (Eds.), Proceedings of the Pro Mare Symposium on Polar Marine Ecology, Trondheim, Norway, pp. 19-31.

Rudels, B., Peter Jones, E.P., Schauer, U., Eriksson, P., 2004. Atlantic sources of the Arctic Ocean surface and halocline waters. Polar Research 23 (2), 181–208.

Saito, K., Taniguchi, A., 1978. Phytoplankton communities in the Bering Sea and adjacent Seas. II: Spring and summer communities in seasonally ice-covered areas. Astarte 11 (1), 27-35.

Sathyendranath, S., Lazzara, L., Prieur, L., 1987. Variations in the spectral values of specific absorption of phytoplankton. Limnology and Oceanography 32 (2), 403-415.
Sherr, E.B., Sherr, B.F., Wheeler, P.A., Thompson, K., 2003. Temporal and spatial variation in stocks of autotrophic and heterotrophic microbes in the upper water column of the central Arctic Ocean. Deep-Sea Research I 50, 557–571.

Smyth, T.J., Tyrrell, T., Tarrant, B., 2004. Time series of coccolithophore activity in the Barents Sea, from twenty years of satellite imagery. Geophysical Research Letters 31, L11302; 11301-11304.

Stedmon, C.A., Markager, S., 2001. The optics of chromophoric dissolved organic matter (CDOM) in the Greenland Sea: An algorithm for differentiation between marine and terrestrially derived organic matter. Limnology and Oceanography 46 (8), 2087-2093.

Townsend, D.W., Rebuck, N.D., Thomas, M.A., Karp-Boss, L., Gettings, R.M., 2010. A changing nutrient regime in the Gulf of Maine. Continental Shelf Research 30, 820-832.

von Quillfeldt, C.H., 2000. Common Diatom Species in Arctic Spring Blooms: Their Distribution and Abundance. Botanica Marina 43, 499-516.

Winter, A., Jordan, R.W., Roth, P.H., 1994. Biogeography of living coccolithophores in ocean waters. In: Winter, A., Siesser, W.G. (Eds.), Coccolithophores. Cambridge University Press, New York, pp. 161-177.

Ziveri, P., Baumann, K.-H., Bockel, B., Bollmann, J., Young, J.R., 2004. Biogeography of selected Holocene coccoliths in the Atlantic Ocean. In: Thierstein, H.R., Young, J.R. (Eds.), Coccolithophores: From molecular processes to global impact. Springer-Verlag, Berlin Heidelberg, pp. 403-428.
Fig. 1- (A) General study area of cruise #1101 of the \textit{USCGC Healy 1101}. (B) Cruise track for Healy #1101 in vicinity of under-ice bloom. Color of data points represents calendar day during 2011 that positions were occupied. Station numbers for every fifth station are shown in yellow. Blue dashed lines show southerly extent of ice sheet as estimated from MODIS imagery, as given by Arrigo (2012). Blue numbers next to blue dashed lines give the specific calendar day that the ice edge was estimated. (C) Along-track temperature (°C) from ship’s flow-through seawater system (depth = 5m) directed through Balch flow-through system. The position of the ice edge on day 189 (July 8, 2011) is designated with the blue dashed line. Isopleths of temperature calculated using Ocean Data View are shown in black contour lines. The white contour line is the position of the -1°C isotherm, the approximate location where Winter Water reached a depth of 5m. The position of the ice edge on day 182 is shown with the blue dashed line for reference. (D) Along-track surface salinity data with same temperature and ice edge isopleths as shown in panel C.

Fig. 2- Underway chlorophyll $a$ absorption and fluorescence properties of the under-ice algal bloom. (A) Chlorophyll $a$ calculated from underway chlorophyll fluorescence, calibrated using shipboard discrete chlorophyll measurements (ug L$^{-1}$); (B) Particulate absorption at 440nm ($a_{p440}$; m$^{-1}$) calculated as the difference between total absorption and absorption following filtration of $<2\mu$m diameter particles; (C) Chlorophyll-specific particulate absorption at 440nm, $a_{p440}^* [m^2 (mg Chl. a)^{-1}]$ calculated by normalizing values of $a_{p440}$ by the chlorophyll concentration; (D) Dissolved ($<0.2\mu$m) absorption at 412nm normalized to total absorption (particulate and dissolved material) at 412 nm ($a_{g412}/a_{pg412}$); (E) FDOM fluorescence (calibrated to quinine sulfate); (F) Relative FDOM fluorescence yield calculated as the FDOM fluorescence normalized to absorption of particulate plus dissolved matter at
412nm. In all panels, isopleths of temperature are shown in black contour lines. The white contour line is the position of the -1°C isotherm, the approximate location where Winter Water reached a depth of 5m. All panels also show the position of the ice edge on day 182 as a blue dashed line for reference.

Fig. 3- (A) Particle absorption at 440nm (m⁻¹; calculated as the difference between total absorption – dissolved absorption) plotted against the concentration of chlorophyll $\text{a}$ (mg m⁻³). (B) Particulate absorption at 412nm plotted against the concentration of chlorophyll $\text{a}$ (mg m⁻³). (C) Particulate absorption at 412nm plotted against particulate absorption at 440nm. (D) Dissolved absorption at 412nm plotted against the concentration of chlorophyll $\text{a}$ (mg m⁻³). Least-squares linear regression lines and fit equations given in panels. Values in square brackets represent the standard error of each of the fitted coefficients. Degrees of freedom (DF), F statistic for the least-squares fit line and probability (P) of estimating this value of F by chance is also given. Statistics also summarized in Table 1.

Fig. 4- Optical properties of the study area. (A) Slope of the absorption spectrum between 412nm and 440nm for dissolved material (<0.2um; $S_g$ (per nm)). (B) Slope of the absorption spectrum between 412nm and 440nm for dissolved plus particulate material ($S_{pg}$ (per nm)). (C) CDOM fluorescence (FDOM; QSU). (D) Fluorescence yield of FDOM (calculated as FDOM/$a_{g412}$; relative units). In all panels, isopleths of temperature and the ice edge on day 182 are shown for reference as in Fig. 1C.

Fig. 5- Variability in FDOM and fluorescence yield. (A) FDOM variability as a function of $a_{g412}$. (B) FDOM variability as a function of chlorophyll concentration. (C) Relative fluorescence yield of FDOM and detritus as a function of the concentration of chlorophyll $\text{a}$. 

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Relative fluorescence yield of FDOM and detritus shown as a function of the slope of the absorption spectrum between 412 and 440 nm (for both dissolved matter, $S_g$). Least-squares linear, power or exponential regression lines and fit equations given in all panels. Values in square brackets represent the standard error of each of the fitted coefficients. Coefficients of correlation, degrees of freedom (DF), F statistic for the least-squares fit line and probability ($P$) of estimating this value of F by chance is also given. See also Table 1.

Fig. 6- Underway scattering and attenuation properties of under-ice algal bloom. (A) $b_{b'531}$ (m$^{-1}$); (B) $b_{bpot531}$ (m$^{-1}$); (C) $b_{b'531}/b_{bpot531}$ (unitless); (D) $b_{p531}$ (m$^{-1}$); (E) backscattering probability ($b^{-}_b = b_{bp}/b_{p'}$, unitless); and (F) beam attenuation at 531 nm ($c_{p531}$; m$^{-1}$). In all panels, isopleths of temperature and the ice edge on day 182 are shown for reference as in Fig. 1C.

Fig. 7- Discrete measurements of PIC and POC through under-ice algal bloom. (A) PIC ($\mu$M L$^{-1}$); (B) POC ($\mu$M L$^{-1}$) and (C) BSi. The -1.6°C isotherm is indicated on each section to show the position of the Winter Water. Two vertical red lines represent where the ship course changed at the offshore extremes of each transect. Blue bar over panel shows extent of ice cover during the transect.

Fig. 8- Discrete measurements of carbon and chlorophyll ratios through under-ice algal bloom. (A) PIC:POC; (B) POC/PON (molar) and (C) POC/Chlorophyll $a$ (g:g). The -1.6°C isotherm is indicated on each section to show the position of the Winter Water. Two vertical red lines represent where the ship course changed at the offshore extremes of each transect.
Fig. 9- Nutrient sections through under-ice algal bloom. (A) Nitrate concentration (μM); (B) Silicate concentration (μM) and (C) Residual nitrate concentration (nitrate-silicate; μM). The -1.6°C isotherm is indicated on each section to show the position of the Winter Water. Two vertical red lines represent where the ship course changed at the offshore extremes of each transect.

Fig. 10- Carbon fixation and carbon-specific growth rates for particulate organic and inorganic carbon. (A) Average photosynthesis (mg m⁻³ d⁻¹); (B) Average calcification (mg m⁻³ d⁻¹); (C) μPOC (d⁻¹); (D) μPIC (d⁻¹). The -1.6°C isotherm is indicated on each section to show the position of the Winter Water. Two vertical red lines represent where the ship course changed at the offshore extremes of each transect. Blue bar over panel shows extent of ice cover during the transect.

Fig. 11- Scanning electron micrographs from under-ice algal bloom: station 56, 1.5m depth under ice: (A) Miscellaneous diatoms at low magnification, (B) Higher magnification view showing Fragilariopsis sp., Chataetocerous sp. and Thalassiosira sp. diatoms (possibly T. nordenskioeldii), (C-E) Fragilariopsis sp. plus two species of Thalassiosira sp. diatoms (possibly T. hyalina and T. nordenskioeldii), (F) Chaetocerous sp. diatom, (G, H) Emiliania huxleyi detached coccoliths. Scale bars shown for reference in each panel in lower right.

Fig. 12- (A) Particulate absorption at 440 nm normalized to mean absorption from 412-715 nm calculated according to Ciotti et al. (2002) calculated according to their equation 1. (B) Fraction of phytoplankton that are picoplankton (Sf) calculated according to equation 3 of Ciotti et al. (2002) for measurements at 440nm. See text for details. In all panels, isopleths of temperature and the ice edge on day 182 are shown for reference as in Fig. 1C.
| Figure | Dependent variable (X axis) | Dependent variable Units | Independent variable (Y axis) | Independent variable Units | SE of Y prediction | Type of fit** | Slope (m) | SE slope | Intercept (b) | SE intercept | Exponent (c) | SE exponent | r² | DF | Fstat |
|--------|----------------------------|--------------------------|-------------------------------|---------------------------|-------------------|----------------|----------|---------|-------------|-------------|------------|-------------|-----|----|--------|
| 3A     | Chlorophyll a mg m⁻³ | a₃₄₄₀ m⁻¹ | 0.0175 | Linear | 0.027 | 9.6x10⁻⁵ | 0.0023 | 4.28x10⁻⁴ | na | na | 0.975 | 2072 | 80477 |
| 3B     | Chlorophyll a mg m⁻³ | a₄₁₂ m⁻¹ | 0.0266 | Linear | 0.025 | 1.46x10⁻⁴ | 0.005 | 6.49x10⁻⁴ | na | na | 0.933 | 2075 | 29077* |
| 3C     | a₃₄₄₀ m⁻¹ | a₄₁₂ m⁻¹ | 0.0183 | Linear | 0.926 | 3.20x10⁻⁵ | na | na | na | na | 0.975 | 2073 | 80993* |
| 3D     | Chlorophyll a mg m⁻³ | a₄₁₂ m⁻¹ | 0.0334 | Linear | 0.004 | 1.69x10⁻⁴ | 0.0966 | 7.92x10⁻⁴ | na | na | 0.233 | 2231 | 676* |
| 5A     | a₄₁₂ m⁻¹ | FDOM QSU | 0.222 | Linear | 3.829 | 0.125 | 2.326 | 0.014 | na | na | 0.305 | 2163 | 949* |
| 5B     | Chlorophyll a mg m⁻³ | FDOM QSU | 0.0261 | Power | 2.796 | 0.004 | na | na | 0.051 | 9.15 x10⁻⁴ | 0.597 | 2163 | 3208* |
| 5C     | Chlorophyll a mg m⁻³ | FDOM/a₄₁₂ QSU⁻m | 0.112 | Power | 25.627 | 0.152 | na | na | 0.256 | 0.107 | 39 | 0.252 | 2161 | 759* |
| 5D     | S₄₁₂⁻₄₄₀ nm⁻¹ | FDOM/a₄₁₂ QSU⁻m | 0.109 | Exponential | 25.649 | 6.11x10⁻⁴ | na | na | 0.867 | 39.55 | 9 | 0.33 | 2154 | 14022* |

* Significance = P<0.001

** Different model fits: Linear model Y=mX+b; Power model Y=mX²; Exponential model Y = me^(cX) where e is Euler's number, 2.71828

Table 1- Statistics of least square fits shown in Figures 10 and 12 this study.
Table 2: Integrated chlorophyll a plus mean primary production and calcification (measured with the microdiffusion technique in triplicate) for stations shown in Fig. 1B. Carbon fixation normalized to total phytoplankton biomass (as chlorophyll) is also given for both photosynthesis and coccolithophore calcification. “Zero” values for calcification indicate that calcification was statistically not different from zero.

| Station | Date     | Year | Time  | Latitude    | Longitude | Int. Chl a | Int. P | Int. C | Int. C(Int. Chl a)^−1 | Int. P (Int. Chl a)^−1 | Int. C (Int. Chl a)^−1 |
|---------|----------|------|-------|-------------|-----------|------------|--------|--------|-----------------------|-----------------------|-----------------------|
| 46.01   | 7/3/2011 | 184.99 | 23:45 | 72.02       | 165.35    | 23.1      | 21.18  | 24.1153% | 755                   | 0.0870                |                       |
| 55.01   | 7/5/2011 | 186.13 | 3:00  | 72.63       | 163.73    | 26.22     | 1086.7 | 1.24%   | 2.61                   | 0.005                 |                       |
| 56.01   | 7/6/2011 | 167.10 | 2:23  | 73.17       | 163.43    | 490.4     | 2695.7 | 0.33%   | 5.83                   | 0.020                 |                       |
| 57.02   | 7/7/2011 | 188.07 | 1:38  | 73.72       | 161.28    | 69.7      | 182.1  | 0.00%   | 2.61                   | 0.000                 |                       |
| 61.02   | 7/9/2011 | 190.91 | 21:54 | 72.24       | 162.29    | 137.6     | 640.2  | 3.20%   | 4.69                   | 0.023                 |                       |
| 90.02   | 7/11/2011| 192.12 | 2:58  | 72.96       | 160.72    | 147.3     | 37.7   | 1.55%   | 5.91                   | 0.006                 |                       |
| 99.01   | 7/12/2011| 193.05 | 1:09  | 73.38       | 160.06    | 3.5       | 49.0   | 0.23%   | 5.79                   | 0.027                 |                       |
| 100.01  | 7/13/2011| 194.13 | 3:03  | 73.70       | 160.28    | 26.1      | 63.5   | 0.27%   | 5.24                   | 0.107                 |                       |
| 103.01  | 7/15/2011| 196.10 | 2:23  | 72.60       | 153.34    | 12.9      | 53.0   | 0.00%   | 4.17                   | 0.000                 |                       |
| 166.01  | 7/23/2011| 201.95 | 22:52 | 71.35       | 130.13    | 154.5     | 794.1  | 0.76%   | 5.14                   | 0.005                 |                       |
Figure A: Chl (mg m⁻³) distribution.
Figure B: $a_p 440$ (m⁻¹) distribution.
Figure C: $a_g 412$ (m⁻¹) distribution.
Figure D: $a_{pg} 412$ (m⁻¹) distribution.
Figure E: $a_{pg} 440$ (m² [mg chl a⁻¹]) distribution.

Longitude
Fig. 7
