

This discussion paper is/has been under review for the journal Biogeosciences (BG).
Please refer to the corresponding final paper in BG if available.

Not all calcite ballast is created equal: differing effects of foraminiferan and coccolith calcite on the formation and sinking of aggregates

K. Schmidt^{1,*}, C. L. De La Rocha², M. Gallinari², and G. Cortese³

¹Faculty of Mathematics and Natural Sciences, University of Groningen, the Netherlands

²CNRS UMR 6539, Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, Plouzané, France

³GNS Science, Lower Hutt, New Zealand

* now at: School of Environmental Science, University of East Anglia, UK

Received: 26 August 2013 – Accepted: 9 September 2013 – Published: 10 September 2013

Correspondence to: C. L. De La Rocha (christina.delarocha@univ-brest.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

BGD

10, 14861–14885, 2013

Not all calcite ballast
is created equal

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Correlation between particulate organic carbon (POC) and calcium carbonate sinking through the deep ocean has led to the idea that ballast provided by calcium carbonate is important for the export of POC from the surface ocean. While this idea is certainly to some extent true, it is worth considering in more nuance, for example, examining the different effects on the aggregation and sinking of POC of small, non-sinking calcite particles like coccoliths and large, rapidly sinking calcite like planktonic foraminiferan tests. We have done that here in a simple experiment carried out in roller tanks that allow particles to sink continuously without being impeded by container walls. Coccoliths were efficiently incorporated into aggregates that formed during the experiment, increasing their sinking speed compared to similarly sized aggregates lacking added calcite ballast. The foraminiferan tests, which sank as fast as 700 m d^{-1} , became associated with only very minor amounts of POC. In addition, when they collided with other, larger, foraminiferan-less aggregates, they fragmented them into two smaller, more slowly sinking aggregates. While these effects were certainly exaggerated within the confines of the roller tanks, they clearly demonstrate that calcium carbonate ballast is not just calcium carbonate ballast- different forms of calcium carbonate ballast have notably different effects on POC aggregation, sinking, and export.

1 Introduction

The export of particulate organic carbon (POC) to the deep ocean prior to its oxidation back to carbon dioxide (CO_2) plays a critical role in the control of atmospheric concentrations of CO_2 (Broecker, 1982; Parekh et al., 2006). But only a small fraction of the carbon fixed into POC in surface waters is exported below 1500 m and therefore excluded from exchange with the atmosphere for time periods longer than a few hundred years (Suess, 1980; Martin et al., 1987; Antia et al., 2001). This small fraction of material escapes from food webs, efficient at retaining and oxidizing organic matter in the

BGD

10, 14861–14885, 2013

**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



upper ocean, largely through the formation and sinking of aggregates larger than 1 mm, including those made primarily of phytoplankton and detritus (Aldredge and Silver, 1988; Kiøboe, 2001; Turner, 2002; Boyd and Trull, 2007; Giudi et al., 2008; Burd and Jackson, 2009; McDonnell and Buesseler, 2010; Ebersbach et al., 2011). In the deep sea, sinking fluxes of POC and minerals (especially calcium carbonate) are strongly correlated, suggesting that ballasting by minerals also plays a role in POC export. This has led to two converse, but ultimately related suggestions. First, that because the density of POC is similar to that of seawater, POC is not dense enough to sink without ballast. Second, despite being denser than seawater, typical mineral particles in the ocean are too small to sink on their own; their export is dependent upon incorporation (with particulate organic matter) into aggregates larger than 1 mm (Deuser et al., 1981; Armstrong et al., 2002; François et al., 2002; Klaas and Archer, 2002; Passow 2004; Passow and De La Rocha 2006; De La Rocha et al., 2008; Thomalla et al., 2008; Engel et al., 2009a, b; Fischer and Karakaş, 2009; Iversen et al., 2010).

Incorporation into aggregates of coccoliths, small scales of calcite produced by coccolithophores, is known to decrease aggregate size but nonetheless increase aggregate sinking velocity (De La Rocha et al., 2008; Engel et al., 2009b; Iversen and Ploug, 2010; Sanders et al., 2010), supporting the notion that POC and minerals need each other to sink out of the surface ocean. However, not all pelagic calcium carbonate is in the form of coccoliths. For example, tests of planktonic foraminiferans make up roughly half of the calcium carbonate settling through the deep sea (Schiebel, 2002). Planktonic foraminiferan tests are large and, devoid of organic matter following gametogenesis, sink with speeds up to or even exceeding 1000 m d^{-1} (Honjo et al., 2008). The shear associated with such fast sinking should remove adhering organic matter, preventing its export from the upper ocean in association with sinking foraminiferan tests. Thus while a significant portion of the calcite exported from the surface ocean should enable, enhance, or at least be associated with sinking fluxes of POC, the other significant portion of sinking calcite should have little influence over POC export.

In order to investigate the possibility that calcite in the form of coccoliths has a different effect on the character and sinking speed of aggregates than calcite in the form of foraminiferan tests, we allowed diatom aggregates to form in cylindrical rolling tanks in the presence of foraminiferan tests or coccoliths (or neither) and observed the difference in the number, size, mass, and sinking speed of the resulting aggregates.

2 Materials and methods

2.1 Experimental setup

This experiment was conducted in a set of cylindrical 4.5L tanks held in rotation on motorized roller tables so that particles could sink unimpeded by container walls for the duration of the experiment (Shanks and Trent, 1980; Passow and De La Rocha, 2006; LeMoigne et al., 2013). Tanks were filled with a culture of the diatom *Chaetoceros gracilis* that had been grown in *f/2* medium (Guillard, 1975) made up in filtered seawater (0.6 μm) for 7 days at 13°C under a light:dark cycle of 14 h : 10 h. The cell concentration in the final volume was 1.5×10^5 cells mL^{-1} . Three different treatments were set up in triplicate (although a number of these replicates were lost to accidents during the experiment): the phytoplankton culture on its own (Phyto), the culture plus 4.6 mg L^{-1} of cleaned coccoliths (Cocco), and the culture plus 4.6 mg L^{-1} of cleaned foraminiferan tests (Foram).

The suspension of coccoliths was prepared from Cretaceous (Maastrichtian) chalk from the cliffs of Rügen, Germany. The chalk was disaggregated, soaked overnight in a solution of 0.6% bleach (to remove remnant organic matter), and rinsed multiple times with Milli-Q water. The calcite was suspended in water, and larger particles were allowed to sink out. A similar suspension used by De La Rocha et al. (2008) consisted of coccoliths generally $< 5 \mu\text{m}$ in diameter and smaller calcium carbonate debris.

The foraminiferan tests that were used in the Foram treatment were taken from a Deep Sea Drilling Project (DSDP) sample, officially discarded due to a buckled core

BGD

10, 14861–14885, 2013

Not all calcite ballast
is created equal

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



liner. The material, Pliocene in age, came from Leg 29 (Station 284, 10-6, 140–150 cm) from the Challenger Plateau (40°30.48' S, 167°40.81' E; 1066 m b.s.l.) west of New Zealand. This material was sieved and intact foraminiferan tests > 250 μm in size were selected via picking with the aid of a binocular microscope. Like the coccoliths, the foraminiferan tests were cleaned by soaking overnight in 0.6% bleach followed by multiple rinses with Milli-Q water.

Following filling with the phytoplankton culture and, where applicable, addition of the calcium carbonate, the rolling tanks were immediately transferred onto the rolling tables and rotated at 3 rpm. The tanks were kept in the dark at 16 °C for 48 h to allow aggregates to form prior to sampling.

2.2 Sampling and analysis

At the beginning of the experiment (T_0), samples of material suspended in the water in the tanks were taken for particulate organic carbon and nitrogen (POC and PON), particulate inorganic carbon (PIC), transparent exopolymer particles (TEP), and biogenic silica (bSiO₂).

After 48 h of rotation (T_f), each tank was taken down individually from the roller table and put to rest flat side down. Each tank was left rotating on the table until it was its turn to be sampled from. After aggregates were allowed to settle for roughly 15 min, a photograph of the tank bottom was made for later counting and sizing of the aggregates using the ImageJ program (Version 1.44 p). Due to the amount of work involved and the loss of some replicate tanks for some of the treatments, this counting and sizing was done from one tank for each treatment. At least 10 aggregates per tank were removed by hand using a plastic, 10 mL, serological pipette whose conical tip had been sawed off. These aggregates were gently transferred into a graduated glass cylinder filled with filtered seawater at the temperature of the room the roller tables were in. The time the aggregates needed to sink a marked distance was timed using a stopwatch and the size of these aggregates was noted against a grid. After the sinking speed measurements for each tank were completed, all visible aggregates > 1 mm in the tank were

collected and combined to form a slurry which was subsampled for POC, PON, PIC, TEP, and bSiO₂. The material remaining in suspension in the tank (termed background water in this manuscript) was also sampled for these parameters.

Concentrations of POC and PON were determined according to Lorrain et al. (2003).

5 Samples of 5–20 mL were filtered gently (< 150 mm Hg) onto pre-weighed, pre-combusted (4 h at 500 °C) GF/F filters (Whatman) and rinsed once with Milli-Q water to remove seasalt. Filters were dried at 60 °C for at least 24 hours and stored until analysis. Immediately prior to analysis, filters were weighed again and then decarbonated via fuming with concentrated hydrochloric acid in a desiccator for 4 h. Samples were
10 then dried overnight at 60 °C and analyzed with a Perkin-Elmer 2400 CHN elemental analyzer using atropine (≥ 99%, Sigma Aldrich) as the calibration standard.

Particulate inorganic carbon (PIC) was sampled and analyzed as described in Poulton et al. (2006). Samples of 5–20 mL were gently filtered onto pre-weighed polycarbonate filters (0.4 μm, Cyclopore) and rinsed with Milli-Q water to remove salts then
15 dried at 60 °C for 24 h. Dried filters were digested in 10 mL of 0.4N HNO₃ for 48 h. After filtration, the filtrate was analyzed for Ca (assuming that all PIC was present as CaCO₃) and Na (to verify that there was no Ca contribution from seasalt) by ICP-AES (HORIBA Jobin YVON/ULTIMA 2).

The abundance of transparent exopolymer particles (TEP) was determined following
20 the spectrophotometric method of Passow and Alldredge (1995). TEP was collected by filtering 5-50 mL of sample under low pressure (< 150 mm Hg) onto polycarbonate filters (0.4 μm, Cyclopore) and then stained with 500 μL of an alcian blue solution and rinsed with Milli-Q water. Filters were folded and stored frozen until analysis. For analysis, filters were soaked in 6 mL of 80 % H₂SO₄ for 2 h to dissolve the alcian blue they had retained. The absorbance of the resulting solution was measured at 787 nm
25 using a PRIM Light and Advanced Spectrophotometer Secomam. Unfortunately, we were unable to calibrate the alcian blue solution against xanthan gum. Values for TEP are therefore reported in units of absorption at 787 nm per volume of sample, allowing comparison among the treatments in this experiment.

**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biogenic silica (bSiO₂) was determined according to a method modified from Rague-
neau and Tréguer (1994). Samples of 5–50 mL were filtered onto polycarbonate filters
(0.4 μm, Cyclo-pore) and dried at 60 °C. Biogenic silica was digested in 0.2 M NaOH at
100 °C in polymethylpentene (PMP) tubes. The reaction was stopped after 1 h by ad-
dition of 1 M HCl. After cooling, samples were centrifuged for 15 min at 3000 rpm and
the supernatant retained for measurement of dissolved silicon concentration (DSi). DSi
was measured with a Shimadzu UV 1700 spectrophotometer following the molybdate
blue method of Mullin and Riley (1965).

3 Results

Aggregates formed in all of the rolling tanks during the experiment (Figs. 1–2). The
smallest number of aggregates formed in the Phyto tanks (99 aggregates in Tank 11,
the Phyto tank that was counted). Almost twice as many aggregates formed in the
Cocco tanks (180 Cocco aggregates in Tank 12, the Cocco tank that was counted). The
Foram tanks, which held the greatest number of aggregates, contained two different
types of aggregates (Figs. 1–2). In Tank 7, the Foram tank which was counted, there
were 59 tiny aggregates that consisted of a single foraminiferan test plus a small amount
of particulate organic matter. These aggregates will be referred to as Foram (w/foram)
aggregates. There were also 557 aggregates that lacked a foraminiferan test. These
aggregates will be referred to as Foram (no foram) aggregates.

Per aggregate the Phyto aggregates contained more POC, PON, bSiO₂, and TEP
than aggregates in the other treatments (Fig. 3), although with an average size of
4.9 ± 2.0 mm, they were not significantly larger than the Cocco aggregates, which av-
eraged 4.3 ± 1.3 mm (Figs. 1–2). Unsurprisingly, the Cocco and the Foram (w/foram)
aggregates contained notably greater amounts of PIC than the Phyto aggregates and
the Foram (no foram) aggregates (Fig. 4a).

Because aggregates formed during the experiment from both suspended and sinking
material, concentrations of POC, PON, bSiO₂, PIC, and TEP suspended in the back-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ground water were lower at the end of the experiment than at the beginning (Figs. 4b and 5). Because the foraminiferan tests sank immediately to the bottom of the tanks when the tanks were not in rotation, concentrations of suspended PIC in the Foram treatment were negligible at both T_0 and T_f (Fig. 4b) despite the addition of 4.6 mg L^{-1} of foraminiferan calcite to these tanks. In contrast, the initial concentration of suspended PIC in the Cocco tanks ($0.49 \pm 0.02 \text{ mg L}^{-1}$) is barely distinguishable from the total amount of PIC known to be added as coccoliths (4.6 mg L^{-1} of $\text{CaCO}_3 = 0.55 \text{ mg L}^{-1}$ of PIC), indicating that the coccoliths remained in suspension for a time even in the absence of rotation.

Within the scatter between replicate tanks and the precision of the measurements, there were not significant differences in the ratios of POC to bSiO_2 , to PON, or to TEP in suspension at the beginning of the experiment and in the aggregates that had formed by the end. Likewise, the difference in the POC to dry weight ratio of the calcite-containing aggregates was not much greater than the variability within aggregate types, although there were hints of differences between aggregate types. The Foram (w/foram) aggregates were $5 \pm 1 \%$ POC by weight compared to $9 \pm 4 \%$ for the Cocco aggregates. In contrast, Phyto aggregates, lacking in added PIC ballast, were $17 \pm 4 \%$ POC by weight. Unsurprisingly, ratios of POC to PIC were significantly lower in the Cocco and Foram (w/foram) aggregates than in the Phyto and Foram (no foram) aggregates (Fig. 7).

The different types of aggregates had different relationships between their size (equivalent spherical diameter, ESD) and sinking speed (Fig. 8). The aggregates that formed in the Foram tanks without incorporating foraminiferan tests (the Foram (no foram) aggregates) sank the most slowly, due to the lack of added calcite ballast and to their relatively small size (Fig. 8). Together with the similar calcite-free Phyto aggregates, they showed a relationship between ESD and sinking speed (W , in m d^{-1}) of $W = 70(\text{ESD})^{1.00} \text{ m d}^{-1}$ ($r^2 = 0.82$). The Cocco aggregates sank faster for a given ESD than the Phyto and Foram (no/foram aggregates), showing a relationship between sinking speed and ESD of $W = 21(\text{ESD})^{0.54}$ ($r^2 = 0.55$).

**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Not all calcite ballast
is created equal**

K. Schmidt et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The Foram (w/foram) aggregates, essentially just foraminiferan tests with a small amount of attached particulate organic matter dragging along behind them, sank both the most rapidly (up to 700 m d^{-1}) and the most rapidly for their size. A clear relationship between sinking speed and ESD was not observed for the Foram (w/foram) aggregates, however. This may have been due to the difficulty of discerning differences in the ESD of particles this small and irregularly sized as the result of the variably sized clump of organic matter adhered to their leeward side. Variability in the POC/PIC ratio due to small differences in the amount of adhered organic matter may also have helped to obscure the relationship between ESD and sinking speed in the Foram (w/foram) aggregates.

4 Discussion

4.1 Influence of coccoliths on the formation and size of aggregates in the rolling tanks

Previous observations have shown that high concentrations of suspended ballast minerals ($0.1\text{--}1000 \text{ mg L}^{-1}$) result in notably smaller, more compact aggregates (Passow and De La Rocha, 2006; De La Rocha et al., 2008; Ploug et al., 2008; Engel et al., 2009b; Iversen and Ploug, 2010). In this experiment, which was run at 4.6 mg L^{-1} calcium carbonate, while the Cocco aggregates appeared less “fluffy” than the Phyto aggregates, quantifying the compaction was difficult. The average ESD of the Cocco aggregates ($4.3 \pm 1.3 \text{ mm}$) is not statistically distinguishable from that of the Phyto aggregates ($4.9 \pm 2.0 \text{ mm}$). Neither are the average POC/ESD ratios of the Cocco aggregates ($7 \pm 2 \mu\text{g mm}^{-1}$) and Phyto aggregates ($10 \pm 5 \mu\text{g mm}^{-1}$) statistically distinguishable from each other. The most that can be said is that the Cocco aggregates spanned a slightly narrower size distribution and had proportionally fewer larger aggregates (i.e. 95% of the Cocco aggregates fell within the 2–6.5 mm ESD range while 95% of the Phyto aggregates fell within the range of 2–9 mm) (Fig. 2).

**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Previous work has also noted that addition of high concentrations of ballast minerals can trigger aggregation (Hamm 2002; Le Moigne et al., 2013) in part by increasing the frequency of collisions between particles (Burd and Jackson, 2009). What remains unknown is whether addition of minerals result in an increased amount of aggregation when conditions are already conducive to aggregation. This experiment suggests not. In each rolling tank, 37 to 38 % of the POC suspended at T_0 had become incorporated into aggregates by the end of the experiment regardless of whether the tank contained the 4.6 mg L^{-1} of calcite (Fig. 5). Likewise, the amount of PON, bSiO_2 , and TEP incorporated into aggregates in the different treatments was essentially the same (Fig. 5) even while, necessarily given the experimental design, the amount of PIC contained in aggregates was different from treatment to treatment (Figs. 4 and 7). Although the exact extent of aggregation may represent an equilibrium between aggregation and disaggregation attained in the rolling tanks (where sinking particles are not exported and thus continue to participate in the aggregation process), it is striking that the results were independent of the addition of calcite and the size and number of aggregates formed. If it is interaction between particulate organic matter (POM) and sticky exopolymers like TEP that serve as the “glue” holding the aggregates together that control the overall extent of aggregation, it is interesting that the presence of added calcite particles neither enhanced nor diminished the amount of POM that TEP could bind into aggregates.

Interestingly, TEP was not preferentially incorporated into aggregates relative to POC or bSiO_2 . The mean POC/TEP ratios for aggregates in the different treatments (Fig. 6) are indistinguishable from one another (ANOVA; $\alpha = 0.05$; $p = 0.07$) as are the mean bSiO_2 /TEP ratios (ANOVA; $\alpha = 0.05$; $p = 0.10$). The mean POC/TEP ratios of the aggregates are also indistinguishable from those of the material initially suspended in the rolling tanks and of the material remaining in suspension at the end of the experiment (ANOVA; $\alpha = 0.05$; $p = 0.08$).

This is not what Engel et al. (2002) observed for aggregates formed during a diatom bloom in nutrient-amended unfiltered seawater in an indoor mesocosm. When aggre-

gates began forming on day 16 of their experiment, their POC/TEP ratio was generally higher than that of the background water of the mesocosm. At first glance, this suggests preferential exclusion of TEP from aggregates. It is more likely that photosynthesis by phytoplankton in the aggregates added POC while TEP in the aggregates may have been more easily accessible and consumed over phytoplankton POC by bacteria and microzooplankton. Photosynthesis and preferentially grazing on TEP were not possibilities in the roller tank experiments reported here, as they were conducted in darkness and using filtered seawater in part to avoid such complexity.

4.2 Impact of foraminiferan tests on aggregate size

Contrary to expectations, a small clump of particulate organic matter remained associated with each rapidly sinking foraminiferan test (Figs. 3 and 7). In keeping with the expectation, however, that foraminiferan aggregates would sink too quickly to be stable or long-lived, most of the aggregates that formed within the Foram tanks did not have foraminiferan tests incorporated within them. The large number and small size of these Foram (no foram) aggregates was caused by their frequent collisions with very rapidly sinking foraminiferan tests. These collisions did not result in the incorporation of a foraminiferan test into a Foram (no foram) aggregate, but in the expulsion of some POM from the Foram (no foram) aggregates. Thus a typical collision reduced the size of the Foram (no foram) aggregate by splitting it into one slightly smaller and one very much smaller Foram (no foram) aggregate, both of which would sink more slowly than the original, slightly larger, Foram (no foram) aggregate (Fig. 8).

Although such fragmentation of aggregates by sinking foraminiferan tests may also occur in the ocean, diminishing sinking fluxes of POC (the opposite of the ballast effect) by fragmenting marine snow into smaller, more slowly sinking forms, the destructive effect of the foraminiferan tests was amplified in the confine of the rolling tanks over the 48 h duration of the experiment. In addition, the release of individual foraminiferan tests following gametogenesis (when foraminiferan organic matter is generally given over to the gametes) generally occurs at a few hundred meters depth within the ocean,

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



potentially deeper than the regions of the epipelagic and upper mesopelagic where the highest concentrations of aggregates occur, diminishing the possibility of an aggregate encountering a foraminiferan tests during its lifetime.

4.3 Sinking speeds

5 As noted by previous studies, the sinking speeds of aggregates in this experiment were related to both the size and composition of the aggregates (Ploug et al., 2008; Engel et al., 2009b; Iversen and Ploug, 2010). In keeping with expectations, larger aggregates sank faster, and aggregates laden with coccolith ballast sank faster than similarly sized aggregates without this additional ballast (Fig. 8).

10 The relationship between ESD and sinking speed for the Phyto aggregates and the Foram (no foram) aggregates plotted along the same trend (sinking speed = $70(\text{ESD})^{1.00}$). This reflects that the Phyto and the Foram (no foram) aggregates had essentially the same composition (diatom POM plus bSiO_2 ballast in the form of diatom frustules but no added calcite ballast). This is unsurprising as they were formed over the same time period from the same starting culture of *Chaetoceros gracilis*. The only real difference between the Phyto aggregates and the Foram (no foram) aggregates is their average ESD; the Foram (no foram) aggregates are smaller because of fragmentation during collision with the rapidly sinking foraminiferan tests, as described in Sect. 4.2.

15 This relationship between ESD and sinking speed for the Phyto and Foram (no foram) aggregates is steeper than measured for aggregates of *Skeletonema costatum* formed in notably smaller rolling tanks (1.15 L) by Iversen and Ploug (2010) (Fig. 8). Likewise, the Cocco aggregates from this experiment also show a steeper relationship between ESD and sinking speed than the *S. costatum* plus coccolith-bearing *Emiliania huxleyi* aggregates of Iversen and Ploug (2010) (Fig. 8). The sinking speeds of the *S. costatum* aggregates were measured via a different method, by suspending them in a known vertical, diffuse flow of water (Ploug and Jorgensen, 1999). Although the sedimentation column method used here tends to yield slightly higher estimates of sinking

**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



speed than the flow system (Ploug et al., 2010), the differences in the estimates are too great to be solely ascribed to this. It is more likely that they relate to differences in the character and composition of the aggregates such as their shape, porosity, wet density, and the amount of bSiO₂ ballasting (diatoms of different species or grown under different conditions have vastly different ratios of POC to bSiO₂). Different techniques used to size the aggregates prior to the sinking speed measurement may have also contributed to the different ESD versus sinking speed slopes.

5 Conclusions

This experiment has confirmed a simple principle, that different physical forms of calcium carbonate (e.g., coccoliths versus planktonic foraminiferan tests) should have significantly different effects on the export of POC from the surface ocean to the deep sea. These differences need to be considered if PIC fluxes are used to estimate or improve estimates of POC sinking fluxes into the deep sea and would help to explain regional variability in the relationship between POC and PIC sinking fluxes (Wilson et al., 2012).

Individual coccoliths, such as shed by coccolithophores, become efficiently incorporated into aggregates. Although at high concentrations they may reduce the size of aggregates through compaction and fragmentation, their incorporation into aggregates result in higher sinking speeds (Fig. 8). In this experiment, they neither enhanced nor inhibited the total transfer of suspended POC into aggregates. Overall, coccoliths should increase the export of POC by increasing its sinking velocity, improving its chances of sinking out of the surface ocean before being oxidized back to CO₂ and nutrients.

Foraminiferan tests, on the other hand, sink so rapidly, they are not an efficient vector for the export of POC from the surface ocean. During the experiment, foraminiferan tests became associated with POC at a ratio of roughly 5 g of POC per gram of PIC compared to coccoliths' 9 g g⁻¹ at the same overall PIC concentration and ratio to total POC (Fig. 7). Thus while any POC associated with foraminiferan tests would sink more rapidly out of the surface ocean than that incorporated into aggregates contain-

BGD

10, 14861–14885, 2013

**Not all calcite ballast
is created equal**

K. Schmidt et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ing coccoliths (Fig. 8), it would take a much greater mass of foraminiferan calcite than coccolith calcite per gram of POC to be hastened out of the surface ocean. In addition, any aggregates stuck by a rapidly sinking foraminiferan test would be potentially fragmented into two more slowly sinking particles.

5 *Acknowledgements.* We thank A. Masson and M.-L. Rouget for assistance with analyses. This work was funded by EURO-BASIN (No. 264933), an Integrating Project of the European Community 7th Framework Programme.

References

- 10 Alldredge, A. L. and Silver, M. W.: Characteristics, dynamics and significance of marine snow, *Prog. Oceanogr.*, 20, 41–82, 1988.
- Antia, A. N., Koeve, W., Fischer, G., Blanz, T., Schulz-Bull, D., Scholten, J., Neuer, S., Kremling, K., Kuss, J., Peinert, R., Hebbeln, D., Bathmann, U., Conte, M., Fehner, U., and Zeitschel, B.: Basin-wide particulate carbon flux in the Atlantic Ocean: regional export patterns and potential for atmospheric CO₂ sequestration, *Global Biogeochem. Cy.*, 15, 845–862, 2001.
- 15 Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., and Wakeham, S.G.: A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals, *Deep-Sea Res. II*, 49, 219–236, 2002.
- Boyd, P. W. and Trull, T. W.: Understanding the export of biogenic particles in oceanic waters: Is there consensus?, *Prog. Oceanogr.*, 72, 276–312, 2007.
- 20 Broecker, W. S.: Ocean chemistry during glacial time, *Geochim. Cosmochim. Acta*, 46, 1689–1705, 1982.
- Burd, A. B. and Jackson, G. A.: Particle aggregation, *Annu. Rev. Mar. Sci.*, 1, 65–90, 2009.
- De La Rocha, C. L., Nowald, N., and Passow, U.: Interactions between diatom aggregates, minerals, particulate organic carbon, and dissolved organic matter: Further implications for the ballast hypothesis, *Global Biogeochemical Cycles*, 22, GB4005, doi:10.1029/2007GB003156, 2008.
- 25 Deuser, W. G., Ross, E. H., and Anderson, R. F.: Seasonality in the supply of sediment to the deep Sargasso Sea and implications for the rapid transfer of matter to the deep ocean, *Deep Sea Res. A*, 28, 495–505, 1981.

**Not all calcite ballast
is created equal**

 K. Schmidt et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


- Ebersbach, F., Trull, T. W., Davies, D. M., and Bray, S. G.: Controls on mesopelagic particle fluxes in the Sub-Antarctic and Polar Frontal Zones in the Southern Ocean south of Australia in summer – Perspectives from free-drifting sediment traps, *Deep-Sea Res. II*, 58, 2260–2276, 2011.
- 5 Engel, A., Goldthwait, S., Passow, U., and Alldredge, A.: Temporal decoupling of carbon and nitrogen dynamics in a mesocosm diatom bloom, *Limnol. Oceanogr.*, 47, 753–761, 2002.
- Engel, A., Abramson, L., Szlosek, J., Liu, Z., Stewart, G., Hirschberg, D., and Lee, C.: Investigating the effect of ballasting by CaCO_3 in *Emiliana huxleyi*: II. Decomposition of particulate organic matter, *Deep-Sea Res. II*, 56, 1408–1419, 2009a.
- 10 Engel, A., Szlosek, J., Abramson, L., Liu, Z., and Lee, C.: Investigating the effect of ballasting by CaCO_3 in *Emiliana huxleyi*: I. Formation, settling velocities and physical properties of aggregates, *Deep-Sea Res. II*, 56, 1396–1407, 2009b.
- Fischer, G. and Karakaş, G.: Sinking rates and ballast composition of particles in the Atlantic Ocean: implications for the organic carbon fluxes to the deep ocean, *Biogeosci.*, 6, 85–102, 2009.
- 15 François, R., Honjo, S., Krishfield, R., and Manganini, S.: Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochem. Cy.*, 16, 1087, doi:10.1029/2001GB001722, 2002.
- Giudi, L., Jackson, G. A., Stemmann, L., Miquel, J. C., Picheral, M., and Gorsky, G.: Relationship between particle size distribution and flux in the mesopelagic zone, *Deep-Sea Res. I*, 55, 1364–1374, 2008.
- 20 Guillard, R. R. L.: Culture of marine phytoplankton for feeding marine invertebrates, in: *Culture of Marine Invertebrate Animals*, edited by: Smith, W. L. and Chanley, M. H., Plenum Press, New York, 26–60, 1975.
- 25 Hamm, C. E.: Interactive aggregation and sedimentation of diatoms and clay-sized 700 lithogenic material, *Limnol. Oceanogr.*, 47, 1790–1795, 2002.
- Honjo, S., Manganini, S. J., Krishfield, R. A., and François, R.: Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983, *Prog. Oceanogr.*, 76, 217–285, 2008.
- 30 Iversen, M. H. and Ploug, H.: Ballast minerals and the sinking carbon flux in the ocean: carbon-specific respiration rates and sinking velocity of marine snow aggregates, *Biogeosci.*, 7, 2613–2624, 2010.

**Not all calcite ballast
is created equal**

K. Schmidt et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Iversen, M. H., Nowald, N., Ploug, H., Jackson, G. A., and Fischer, G.: High resolution profiles of vertical particulate matter export off Cape Blanc, Mauritania: Degradation processes and ballasting effects, *Deep Sea Res. I*, 57, 711–784, 2010.

Kjørboe, T.: Formation and fate of marine snow: small-scale processes with large-scale implications, *Sci. Mar.*, 65, 57–71, 2001.

Klaas, C. and Archer, D. E.: Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochem. Cy.*, 16, 1116, doi:10.1029/2001GB001765, 2002.

Le Moigne, F. A. C., Gallinari, M., Laurenceau, E., and De La Rocha, C. L.: Enhanced rates of particulate organic matter remineralization by microzooplankton are diminished by added ballast minerals, *Biogeosciences*, 10, 5755–5765, doi:10.5194/bg-10-5755-2013, 2013.

Lorrain, A., Savoye, N., Chauvaud, L., Paulet, Y.-M., and Naulet, N.: Decarbonation and preservation method for the analysis of organic C and N contents and stable isotope ratios of low-carbonated suspended particulate material, *Anal. Chim. Acta*, 491, 125–133, 2003.

Martin, J. H., Knauer, G. A., Karl, D. M., and Broenkow, W. W.: VERTEX: carbon cycling in the northeast Pacific, *Deep-Sea Res.*, 34, 267–285, 1987.

McDonnell, A. M. P. and Buesseler, K. O.: Variability in the average sinking velocity of marine particles, *Limnol. Oceanogr.* 55, 2085–2096, 2010.

Mullin, J. B. and Riley, J. P.: The spectrophotometric determination of silicate-silicon in natural waters with special reference to sea water, *Anal. Chim. Acta*, 46, 491–501, 1965.

Parekh, P., Dutkiewicz, S., Follows, M. J., and Ito, T.: Atmospheric carbon dioxide in a less dusty world, *Geophys. Res. Lett.*, 33, L03610, doi:10.1029/2005GL025098, 2006.

Passow, U.: Switching perspectives: do mineral fluxes determine particulate organic carbon fluxes or vice versa?, *Geochem. Geophys. Geosyst.*, 5, Q04002, doi:10.1029/2003GC000670, 2004.

Passow, U. and Alldredge, A. L.: Aggregation of a diatom bloom in a mesocosm: The role of transparent exopolymer particles (TEP), *Deep-Sea Res. II*, 42, 99–109, 1995.

Passow, U. and De La Rocha C. L.: Accumulation of mineral ballast on organic aggregates, *Global Biogeochem. Cy.*, 20, GB1013, doi:10.1029/2005GB002579, 2006.

Ploug, H. and Jørgensen, B. B.: A net-jet flow system for mass transfer and microsensor studies of sinking aggregates, *Mar. Ecol. Prog. Ser.*, 176, 279–290, 1999.

**Not all calcite ballast
is created equal**

K. Schmidt et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Ploug, H., Iversen, M. H., and Fischer, G.: Ballst, sinking velocity, and apparent diffusivity within marine snow and zooplankton fecal pellets: Implications for substrate turnover by attached bacteria, *Limnol. Oceanogr.* 53, 1878–1886, 2008.

Ploug, H., Terbrüggen, A., Kaufmann, A., Wolf-Gladrow, D., and Passow, U.: A novel method to measure particle sinking velocity in vitro, and its comparison to three other in vitro methods, *Limnol. Oceanogr., Methods*, 8, 386–393, 2010.

Poulton, A. J., Sanders, R., Holligan, P. M., Stinchcombe, M. C., Adey, T. R., Brown, L., and Chamberlain, K.: Phytoplankton mineralization in the tropical and subtropical Atlantic Ocean, *Global Biogeochem. Cy.*, 20, GB4002, doi:10.1029/2006gb002712, 2006.

Ragueneau, O. and Tréguer, P.: Determination of biogenic silica in coastal waters: applicability and limits of the alkaline digestion method, *Mar. Chem.*, 45, 43–51, 1994.

Sanders, R., Morris, P. J., Poulton, A. J., Stinchcombe, M. C., Charalampopoulou, A., Lucas, M. I., and Thomalla, S. J.: Does a ballast effect occur in the surface ocean?, *Geophys. Res. Lett.*, 37, L08602, doi:10.1029/2010GL042574, 2010.

Schiebel, R.: Planktic foraminiferal sedimentation and the marine calcite budget, *Global Biogeochem. Cy.*, 16, 1065, doi:10.1029/2001GB001459, 2002.

Shanks, A. L. and Trent, J. D.: Marine snow – Sinking rates and potential role in vertical flux, *Deep-Sea Res. A*, 27, 137–143, 1980.

Suess, E.: Particulate organic carbon flux in the oceans- surface productivity and oxygen utilization, *Nature*, 288, 260–263, 1980.

Thomalla, S. J., Poulton, A. J., Sanders, R., Turnewitsch, R., Holligan, P. M., and Lucas, M. I.: Variable export fluxes and efficiencies for calcite, opal, and organic carbon in the Atlantic Ocean: A ballast effect in action?, *Global Biogeochem. Cy.*, 22, GB1010, doi:10.1029/2007GB002982, 2008.

Turner, J. T.: Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms, *Aquat. Microb. Ecol.*, 27, 57–102, 2002.

Wilson, J. D., Barker, S., and Ridgwell, A.: Assessment of the spatial variability in particulate organic matter and mineral sinking fluxes in the ocean interior: Implications for the ballast hypothesis, *Global Biogeochem. Cy.*, 26, GB4011, doi:10.1029/2012GB004398, 2012.

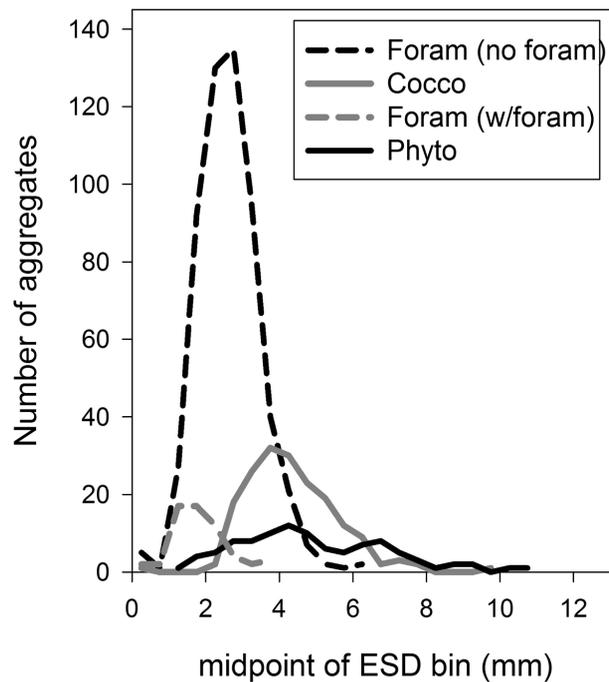


Fig. 2. Frequency of ESDs of aggregates in Tank 11 (Phyto), Tank 7 (Foram), and Tank 12 (Cocco). The ESD bins are 0.5 mm wide.

Not all calcite ballast is created equal

K. Schmidt et al.

[Title Page](#)

[Abstract](#) [Introduction](#)

[Conclusions](#) [References](#)

[Tables](#) [Figures](#)

[◀](#) [▶](#)

[◀](#) [▶](#)

[Back](#) [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Not all calcite ballast is created equal

K. Schmidt et al.

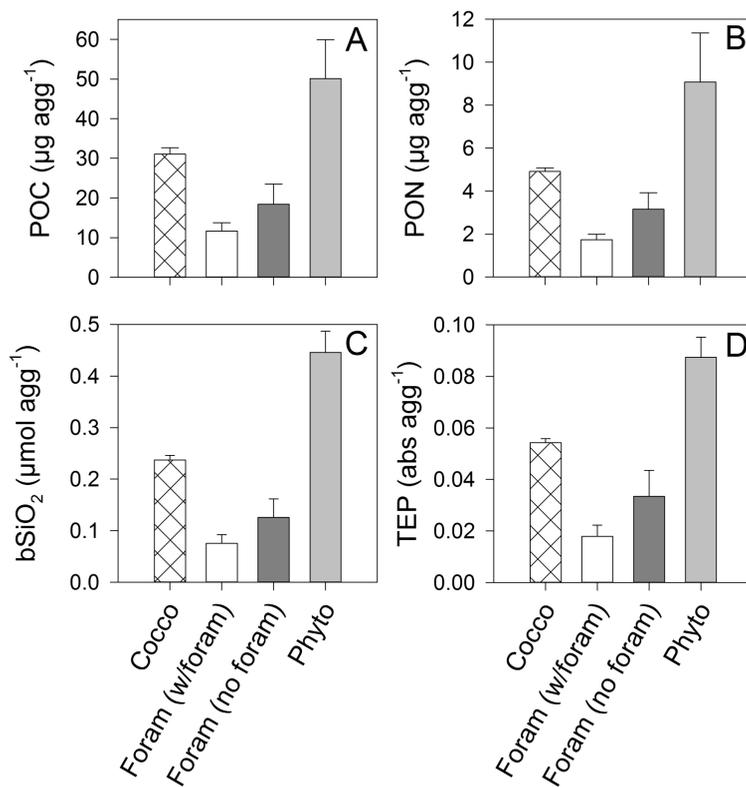


Fig. 3. Average content of (A) POC, (B) PON, (C) bSiO₂, (D) TEP per aggregate for the different types of aggregates formed.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Not all calcite ballast is created equal

K. Schmidt et al.

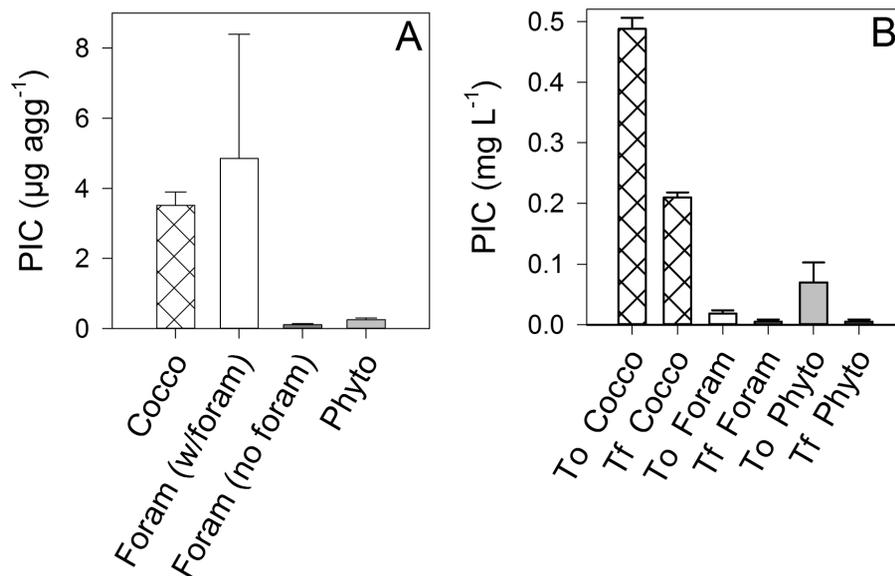


Fig. 4. Concentrations of PIC (in $\mu\text{g C}$) in **(A)** aggregates at the end of the experiment and **(B)** suspended in the water in the tanks of the different treatments at the beginning (T_0) and end (T_f) of the experiment.

Not all calcite ballast is created equal

K. Schmidt et al.

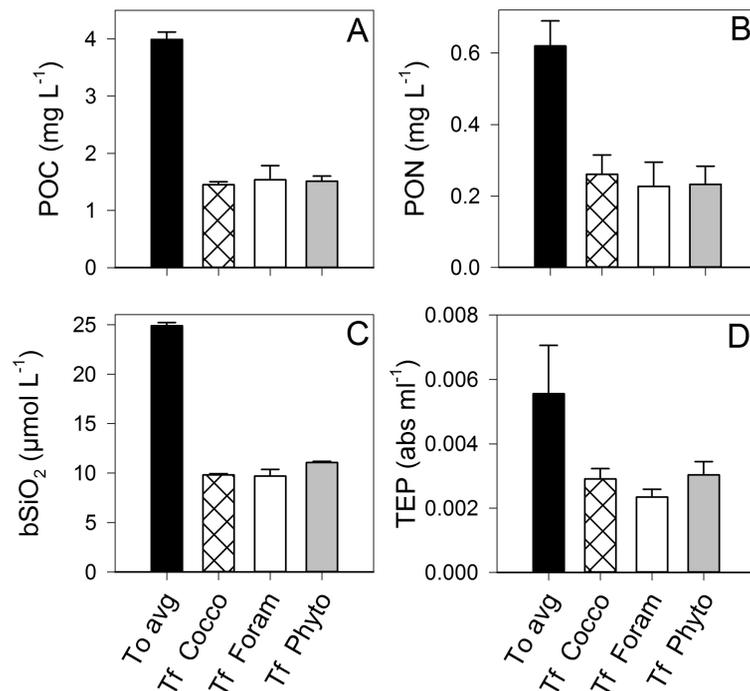


Fig. 5. Concentrations of suspended **(A)** POC, **(B)** PON, **(C)** bSiO₂, and **(D)** TEP at the beginning of the experiment (T₀, representing an average of all three treatments) and at the end of the experiment (T_t, representing an average of the replicate tanks for each treatment).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Not all calcite ballast is created equal

K. Schmidt et al.

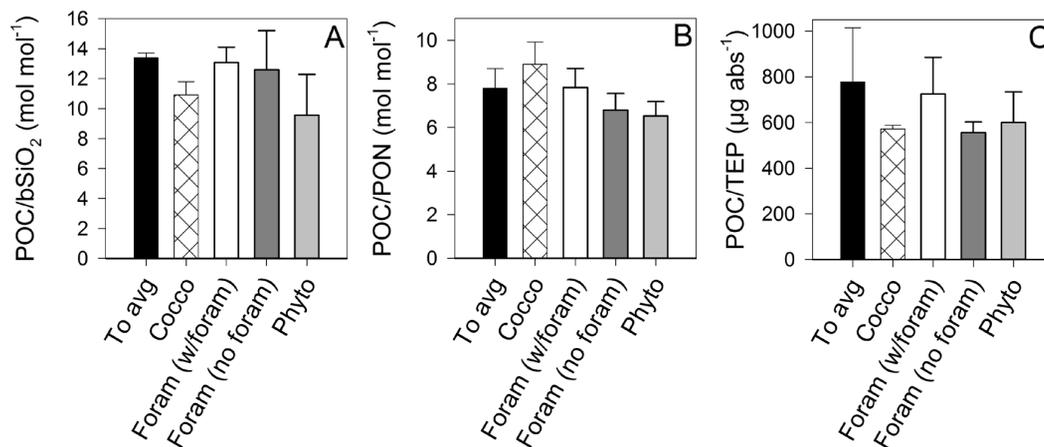


Fig. 6. The ratios of **(A)** POC to bSiO₂, **(B)** POC to PON, and **(C)** POC to TEP in suspension at T_0 (the value reported represents an average of the T_0 samples for all three treatments) and in the aggregates at the end of the experiment.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Not all calcite ballast is created equal

K. Schmidt et al.

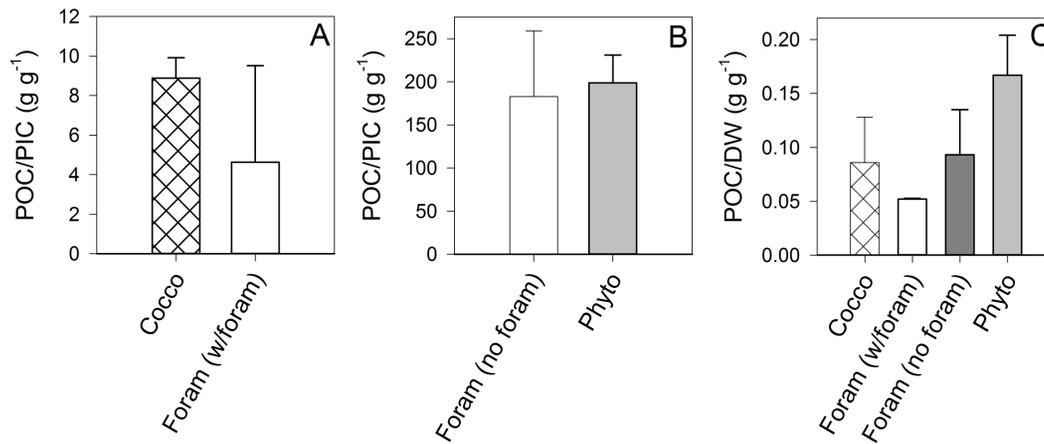


Fig. 7. Ratios of POC/PIC in **(A)** calcite-containing aggregates and in **(B)** aggregates lacking calcite and ratios of **(C)** POC to dry weight in all aggregates.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Not all calcite ballast is created equal

K. Schmidt et al.

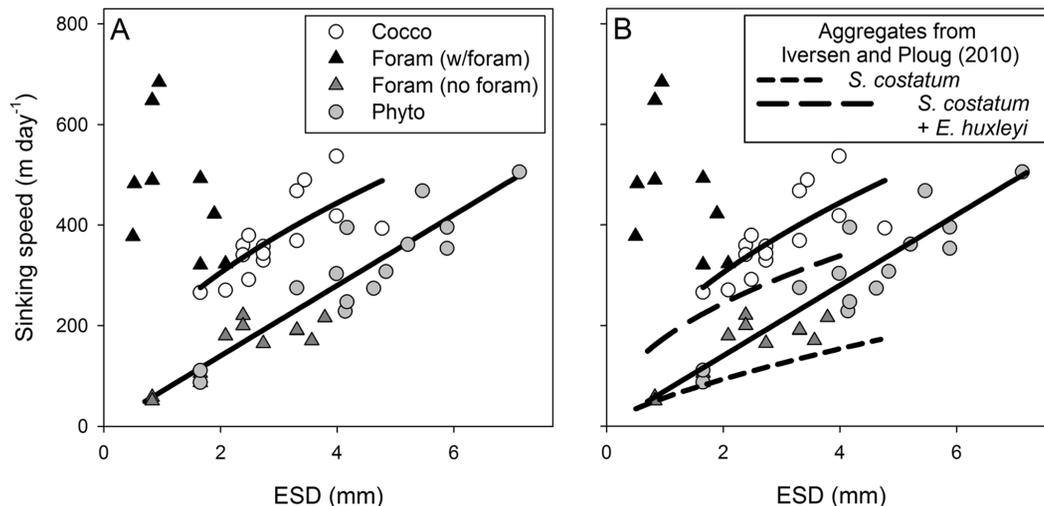


Fig. 8. Sinking speeds versus size (equivalent spherical diameter) of the different types of aggregates formed in this experiment. The curves shown for the aggregates from this experiment are $y = 21(\text{ESD})^{0.54}$ for the Cocco aggregates ($r^2 = 0.55$), and $y = 70(\text{ESD})^{1.00}$ for the Phyto and the Foram (no foram) aggregates taken together ($r^2 = 0.82$). In addition, panel B shows for comparison the relationships reported for *Skeletonema costatum* aggregates and aggregates of a mixture of *S. costatum* and *Emiliana huxleyi* by Iversen and Ploug (2010).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

