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## Interactions between diatom aggregates, minerals, particulate organic carbon, and dissolved organic matter: Further implications for the ballast hypothesis

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[1] Correlations of particulate organic carbon (POC) and mineral fluxes into sediment traps in the deep sea have previously suggested that interactions between organic matter and minerals play a key role in organic matter flux to the deep. Here experiments were carried out in rolling tanks to observe the incorporation of suspended biogenic minerals (calcium carbonate coccoliths or silica diatom frustules) into diatom aggregates and examine their influence on aggregate character. Addition of higher concentrations of suspended minerals to tanks resulted in a decrease in aggregate volume and mass and in an increase in aggregate number. POC to dry weight ratios also declined as mineral concentrations increased, saturating at 2–5 weight percent POC. Large amounts of suspended particulate material, consisting of miniscule aggregates of both inorganic material and organic matter, formed during the experiments. This suggested sizable scavenging of dissolved organic matter into the particulate phase during the experiment in general, and in particular associated with the presence of suspended minerals. Some of the increase in particulate inorganic matter may have been tied to cation crosslinking of the polymerized organic matter. The C to N ratio of this scavenged material was lower in the opal experiments than in the calcium carbonate experiments, suggesting differences in the compounds being formed.

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### 1. Introduction

[2] Rising atmospheric CO<sub>2</sub> concentrations have provoked considerable interest in the marine carbon cycle and in the transfer of carbon, fixed into organic matter, to the deep sea via the biological pump. Although progress has been made toward identifying and describing processes contributing to the transport of organic matter to the deep, a predictive understanding of the flux of organic carbon to the seafloor remains elusive. Thus the discovery of a strong correlation between the flux of particulate organic carbon (POC) and the flux of minerals such as opal (biogenic silica), calcium carbonate, and lithogenic silica (e.g., clay and mineral silicates) into deep sediment traps [Armstrong *et al.*, 2001; François *et al.*, 2002; Klaas and Archer, 2002]

was widely noticed and welcomed as a means of predicting the flux of POC out of the surface ocean.

[3] Because there are significant correlations between the organic and mineral fluxes into deep sediment traps, it was proposed that not only could the sinking flux of minerals be used to predict the POC flux to the deep sea, but that the POC flux to the deep sea is controlled by the sinking flux of minerals [Armstrong *et al.*, 2001; François *et al.*, 2002; Klaas and Archer, 2002]. That the correlation between calcium carbonate and POC fluxes is stronger than the one between opal and POC fluxes was taken to suggest that more than 80% of the POC reaching the deep sea gets there as a result of calcium carbonate “ballast” [Klaas and Archer, 2002]. It was also noted that POC comprises a fairly uniform 5 or so percent of the total dry weight (DW) of material reaching the deep sea.

[4] To explain these observations, the ballast hypothesis calls upon minerals to increase the transmission of POC to the deep by increasing the velocity with which it sinks (by adhering to POC and increasing its density) or by decreasing the rate at which it is remineralized (by providing some sort of protection from microbial degradation). If this interpretation of the correlations and the uniformity of the POC to dry weight ratio is correct, the quantity, mode, location, and seasonality of primary production, the formation of large aggregates (i.e., marine snow) in the surface

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ocean, and the activities of zooplankton and bacteria are unimportant to the overall amount of POC reaching the deep sea. Likewise, it must follow that a decrease in calcium carbonate production by pelagic coccolithophorids due to the rise in atmospheric CO<sub>2</sub> concentrations (a possibility for which there is mixed evidence [Riebesell *et al.*, 2000; Langer *et al.*, 2006]) will decrease the POC flux to depth, providing a positive feedback to rising CO<sub>2</sub> concentrations [Barker *et al.*, 2003; Ridgwell, 2003].

[5] Although the prospect of predicting POC fluxes from mineral fluxes is a simple and attractive one, the initial proposers of the ballast hypothesis themselves recognized that the relationship between minerals and POC is undoubtedly complex [Armstrong *et al.*, 2001; François *et al.*, 2002; Klaas and Archer, 2002]. Among other things, these authors pointed out that flux of minerals to the deep is not an independent variable, given that sinking velocities (and possibly remineralization rates) are likely to be a function of mineral-organic matter ratios. Likewise, they suggested that organic matter is the glue holding sinking organic matter-mineral aggregates together and when its abundance in the sinking particles gets too low, aggregates fall apart and the remaining organic matter and minerals both stop sinking [Armstrong *et al.*, 2001].

[6] Further in this vein, it has been pointed out that it is equally logical (or equally illogical) to conclude from the correlations between mineral and POC fluxes into the deep ocean that the POC fluxes determine the mineral fluxes [Passow, 2004; Passow and De La Rocha, 2006]. Under this scenario, deep and intermediate depth waters must contain minerals which are small enough to have negligible sinking velocities and to thus remain suspended until they are scavenged by sinking aggregates formed in surface waters. The idea that aggregates, consisting of materials such as phytoplankton (predominantly diatoms), fecal pellets, mucous feeding structures of zooplankton such as appendicularians [Allredge and Silver, 1988], and transparent exopolymers (TEP) [Allredge *et al.*, 1993], “clean” the water column by collecting suspended materials as they sink is not new [McCave, 1984; Smetacek, 1985; Hamm, 2002]. Descriptions of aggregates scavenging minerals out of the water column have long existed, especially for coastal areas containing relatively high concentrations of clays [Brzezinski and Nelson, 1995; Kumar *et al.*, 1998; Passow *et al.*, 2001].

[7] Observations of interactions between POC and minerals are needed to test and refine the ballast hypothesis. For example, a set of experiments carried out in rolling tanks with aggregates and minerals (reagent grade calcium carbonate and the clay, illite) showed that as aggregates adsorb more minerals, their POC to DW ratios decrease down to 5 weight % before leveling off [Passow and De La Rocha, 2006]. This POC to DW ratio appears to reflect the saturation of the POC with minerals and would explain the similar limit seen in the sediment trap data. The rolling tank experiments also revealed that the adsorption of minerals onto aggregates decreases their size and eventually fragments them into thousands of small particles, an unexpected result that has significant implications for particle sinking velocities [Passow and De La Rocha, 2006; De La Rocha and Passow, 2007].

**Table 1.** Total Additions and Concentrations of Minerals in Rolling Tanks

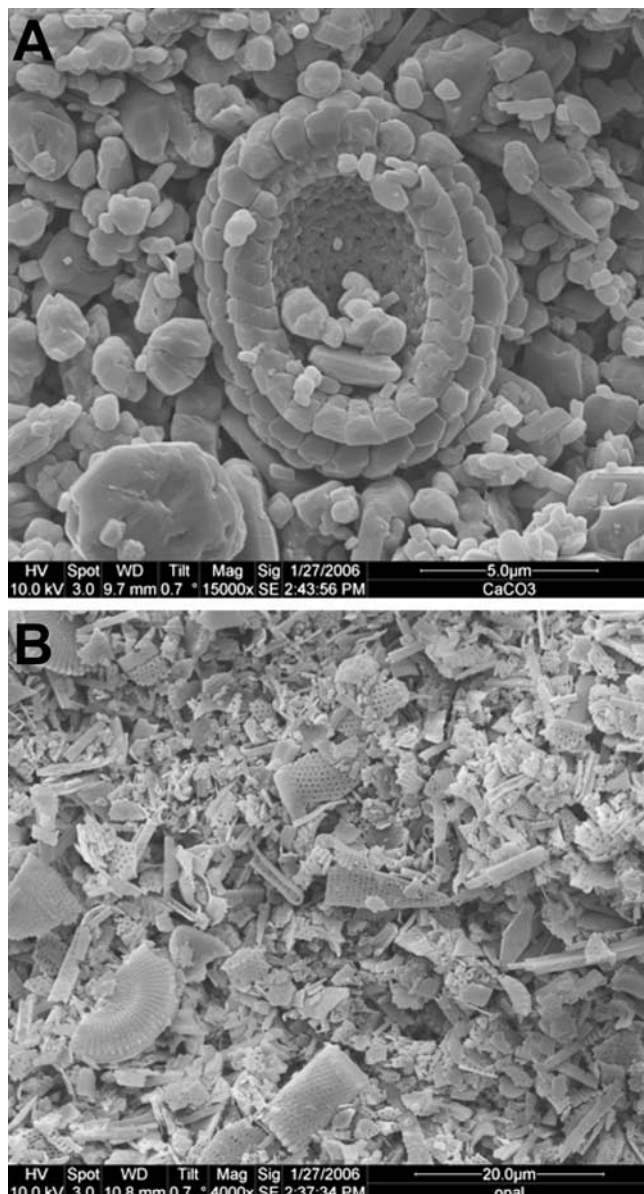
Tank	Tank Volume (L)	CaCO <sub>3</sub> Experiment		SiO <sub>2</sub> Experiment	
		Total Added CaCO <sub>3</sub> (mg)	[CaCO <sub>3</sub> ] (μg L <sup>-1</sup> )	Total Added SiO <sub>2</sub> .nH <sub>2</sub> O (mg)	[SiO <sub>2</sub> .nH <sub>2</sub> O] (μg L <sup>-1</sup> )
1	4.5	0	0	0	0
2	4.0	0.4	100	0.4	100
3	4.5	2	500	2	400
4	4.5	7	1,500	6	1,300
5	4.5	43	9,600	38	8,500
6	4.5	176	39,000	153	34,000

[8] Here we present a follow up to these initial experiments, this time using a coccolith-bearing chalk as a more “natural” source of calcium carbonate than the reagent grade calcium carbonate of the previous experiment. In addition, we investigated for the first time the impact of biogenic silica on aggregates to see if organic matter-silica interactions differ significantly from organic matter-calcium carbonate interactions, as implied by the stronger relationship between calcium carbonate fluxes and POC fluxes into the deep sea. In addition, particulate organic matter (POM) and particulate inorganic matter (PIM) budgets have been monitored over the course of the experiment. This was done more to take organic matter degradation into account, but it turned out to reveal other things entirely.

## 2. Materials and Methods

[9] These experiments investigating the interactions between suspended biominerals (calcium carbonate and silica) and organic aggregates were carried out in cylindrical tanks rotating on rolling tables to emulate the sinking of the material through a water column [Shanks and Edmondson, 1989]. For each experiment, 6 transparent, cylindrical rolling tanks were filled with North Sea seawater that had been filtered through a 0.2 μm cartridge filter. To these tanks, aliquots of a stock solution of suspended calcium carbonate or silica were added to produce suspended mineral concentrations of 0 to 39,000 μg L<sup>-1</sup> (Table 1), which spanned the range from those of middepths in the open ocean, through those of the nepheloid layer and coastal surface waters (up to about 250 μg L<sup>-1</sup>) [Biscaye and Eitrem, 1977; Simpson 1982], up to those of turbid systems like estuaries and the North Sea (which can have suspended mineral concentrations as high as 70,000 μg L<sup>-1</sup>) [Ferrari *et al.*, 2003]. The volume of the rolling tanks was 4.5 L except in the case of Tank 2, which only had a volume of 4 L. Phytoplankton aggregates 3–5 mm long were inoculated into each tank and allowed to interact with the suspended minerals for 2 days. The two experiments (i.e., one for each mineral) were conducted simultaneously with replicate phytoplankton aggregates. Tanks were shaded within a tent of black plastic sheeting and kept in a culture room with the overhead lights off in order to encourage aggregation and prohibit phytoplankton photosynthesis (and production of organic matter).

[10] The phytoplankton aggregates for the experiments were prepared at low light at 15.7°C in several rotating, 8-L cylindrical tanks by incubating concentrated cultures of the



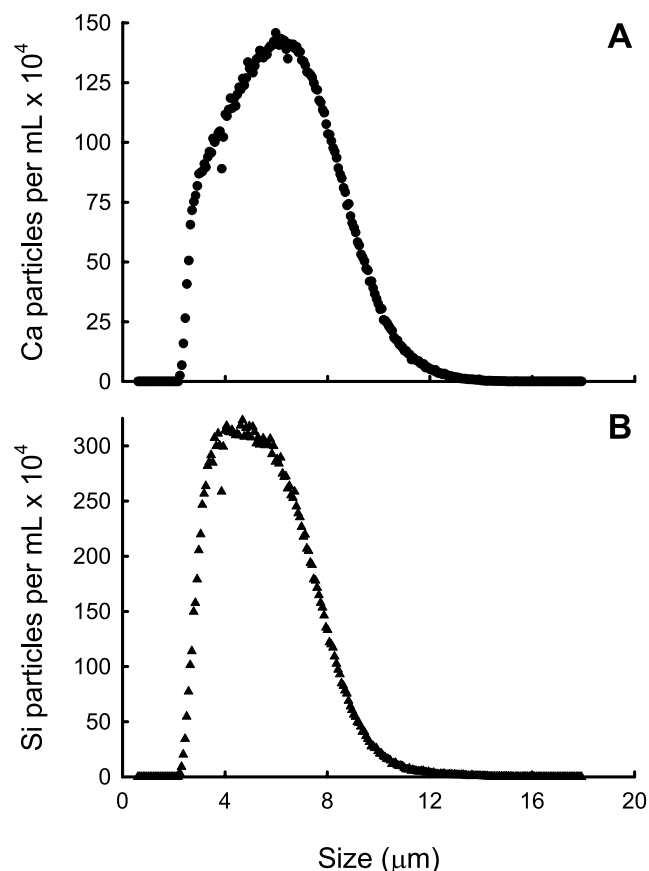
**Figure 1.** Scanning electron microscope scans of the (a) calcium carbonate and (b) silica used in the experiments.

diatoms, *Skeletonema costatum* and *Chaetoceros decipiens* (grown in f/2 medium), and a few milliliters of frozen concentrate of the same species, in sterile, filtered seawater. Through collision of particles settling at different velocities, aggregates of the phytoplankton material were formed [Jackson, 1994]. Approximately 80 aggregates were produced for each experiment.

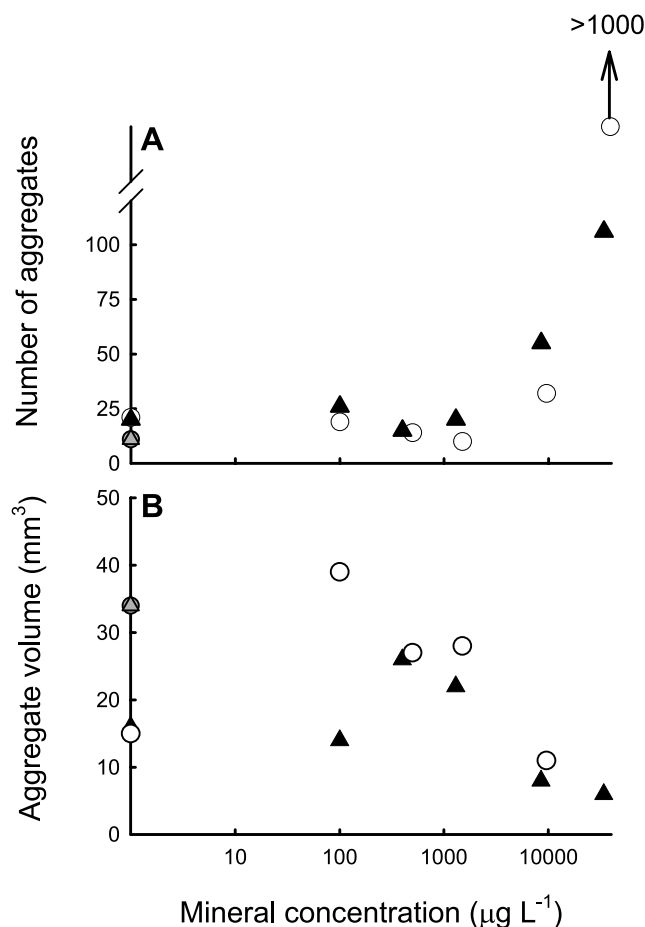
[11] The solution of suspended calcium carbonate was prepared from Cretaceous (Maastrichtian) chalk from the cliffs of Rügen, Germany, on the Baltic Sea. The chalk was disaggregated, soaked overnight in 3.5% sodium hypochlorite solution, and rinsed with deionized distilled water. Particles were suspended in deionized distilled water and only those remaining in suspension after several minutes were used in the experiment.

[12] The solution of suspended silica (opal) was prepared from a freshwater diatomite. The diatomite was wet sieved and the  $<10\ \mu\text{m}$  fraction selected. Minerals were removed from this fraction by centrifuging mixtures of the sieved diatomite and a sodium polytungstate solution adjusted to have a density greater than that of opal but lower than that of silicate minerals. Inspection of the separated opal fraction through a polarizing microscope revealed it to be free of silicate mineral grains. The separated opal fraction was then cleaned for 1 h at  $60^\circ\text{C}$  in a 50:50 (volume to volume) solution of 30% hydrogen peroxide and concentrated HCl. This solution was allowed to cool overnight before collection of the particles through centrifugation and rinsing. Cleaned opal was then suspended in water and only the particles remaining in suspension after several minutes were selected for the experiment.

[13] The concentrated solutions of calcium carbonate and silica consisted largely of coccoliths and smaller calcium carbonate debris (Figure 1a) and fragments of diatom frustules (Figure 1b). These particles were smaller than  $17\ \mu\text{m}$  in diameter and the distribution of sizes in the solutions used to inoculate the experimental tanks with minerals was similar between the calcium carbonate and silica (Figure 2). It should be noted that the asymmetry of the peaks and the lower limits of the size frequency



**Figure 2.** The size distribution of particles in the (a) calcium carbonate and (b) silica stock solutions used to inoculate the rolling tanks with suspended minerals.



**Figure 3.** The (a) total number and (b) average volume of aggregates present at the end of the calcium carbonate (open circles) and silica (solid triangles) experiments. Grey symbols represent the aggregates inoculated into the tanks at the beginning of the experiments.

distributions shown in Figure 2 reflect the lower detection limit of the Coulter counter used to characterize them and not the absence of particles smaller than  $2 \mu\text{m}$ . It should also be noted that the calcium carbonate particles were slightly heavier than the silica particles, at  $6 \times 10^{-11} \text{ g}$  per particle of calcium carbonate versus  $3 \times 10^{-11}$  for the silica. This can be ascribed to a combination of a slightly higher average size for the calcium carbonate particles ( $6.2 \mu\text{m}$  versus  $5.6 \mu\text{m}$ ) and their slightly greater density relative to opal ( $2.7$  to  $2.95 \text{ g cm}^{-3}$  versus  $2.6 \text{ g cm}^{-3}$ ) [Smyda, 1970].

[14] The opal and the calcium carbonate experiments were run simultaneously and inoculated with aggregates from the same initial stock to allow direct comparison of the results of the two experiments. For each experiment, approximately 80 aggregates of generally 3 to 5 mm in length were removed gently from the 8-L tanks with a large bore pipette. These aggregates were placed in petri dishes filled with sterile seawater and their length and width were recorded (<1, 1–3, 3–5, and >10 mm). For each experiment, 15 aggregates were selected and set aside for initial measurements of dry weight (DW), PIM, POM, and POC.

Eleven of the remaining aggregates were transferred into each of the 6 rolling tanks per experiment to which suspended minerals had been added. The tanks containing the minerals and aggregates were rotated at 3.1 rpm for 2 days at  $15.7^\circ\text{C}$  and then the experiment was terminated. At the rotation speed used, aggregates were kept suspended in the tanks, and did not collide with the tank walls.

[15] At the end of the experiment, the number of aggregates greater than 1 mm in length in each tank was counted and the length of each of these large aggregates was noted. Aggregate volumes were calculated as for spheres from the diameter estimates. All aggregates greater than 1 mm in length were collected, transferred onto preweighed, precombusted GFF filters, rinsed with water to remove salts, and then dried. The dry weight of the aggregates was measured for all filters so that a total amount of aggregate dry weight could be obtained. Some of the filters were then analyzed for POC and PON using an elemental analyzer (ANCA SL 20–20); samples containing calcium carbonate were acidified prior to analysis to remove inorganic carbon. The rest of the filters were analyzed for their PIM and POM content via loss on ignition (LOI) at  $500^\circ\text{C}$ .

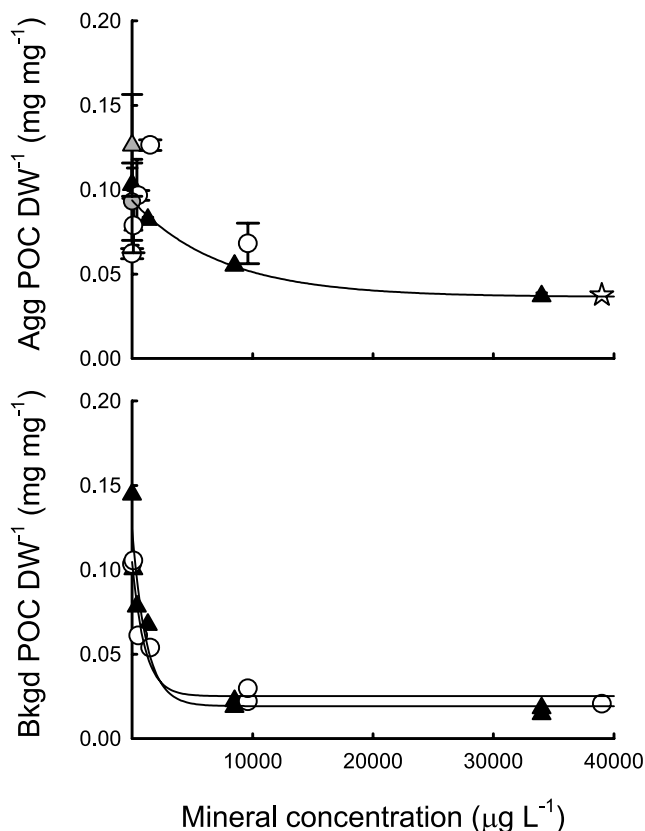
[16] At the end of the experiment in tank 6 of the calcium carbonate experiment, there was a substantial number of aggregates that were small (less than 1 mm in length) but still visible to the naked eye. It was impossible to enumerate these small aggregates, and only a subsample of their total could be collected (using a syringe) for analysis of dry weight, POC, PON, PIM, and POM. Samples of the backgroundwater (and any particles suspended in it) were also collected at the end of the experiment using a syringe. Because the small aggregates were dense enough to sink to the bottom when the tanks stopped rotating, it was possible to obtain a clean sample of the backgroundwater even in tanks in which an abundance of small aggregates was present.

### 3. Results and Discussion

#### 3.1. Comparison With Earlier Experiments

[17] Although these experiments on the interaction of aggregates with suspended minerals were carried out using coccoliths or fragments of diatom opal as the source of minerals, the results obtained reproduce those from an earlier set of experiments investigating the impact of clay and reagent grade calcium carbonate on aggregates [Passow and De La Rocha, 2006]. As with the earlier experiments, the addition of aggregates to seawater containing a high concentration of suspended minerals resulted in the fragmentation of aggregates into a large number of smaller, more compact particles (Figure 3). The POC to dry weight ratio of aggregates dropped with increasing suspended mineral concentration (Figure 4a) and leveled off around the 5 weight percent organic carbon of the previous experiments and as seen for particle fluxes through the deep sea [Armstrong et al., 2001].

[18] In addition to confirming the earlier results obtained with the purified materials, the testing of the biogenic minerals lends confidence that the interactions between aggregates and minerals studied in these experiments rep-



**Figure 4.** The POC to dry weight of (a) macroscopic aggregates in the experiments and (b) miniscule aggregates present in the backgroundwater in the tanks. Symbols are as in Figure 3. In addition, the open star indicates samples of the small aggregates that existed at the end of the experiment in the highest concentrations calcium carbonate tank. All points in Figure 4a have error bars representing the standard deviation of 2–5 replicate samples. The curve fit to the opal data in Figure 4a is  $y = 0.037 + 0.057e^{0.00014x}$  ( $r^2 = 0.90$ ). The curve fit to the opal data in Figure 4b is  $y = 0.019 + 0.11e^{0.00085x}$  ( $r^2 = 0.93$ ). The curve fit to the calcium carbonate data in Figure 4b is  $y = 0.025 + 0.080e^{0.00095x}$  ( $r^2 = 0.95$ ).

resent those that could be occurring in the water column. That aggregate POC to dry weight ratios in these new experiments also flattened out around the 5 weight percent organic carbon observed previously for clay and calcium carbonate additions [Passow and De La Rocha, 2006] and in sediment traps [Armstrong et al., 2001] bolsters the assertion that 5 weight percent POC is the carrying capacity of POC for inorganic minerals [Passow, 2004; Passow and De La Rocha, 2006]. This corroborates the point made by [Armstrong et al., 2001] that the organic matter acts as the “glue” to hold the organic matter-mineral aggregates together and that at a high abundance of minerals, this glue is overwhelmed and the aggregates fall apart.

### 3.2. Production of Tiny Aggregates

[19] By the end of the experiment, a considerable number of aggregates, too small to be seen by the naked eye but

large enough to be collected on GFF filters, was present in the tanks. This can be seen by the large amount of particulate material (8 to 41 mg dry weight) that was suspended in the backgroundwater of each tank at the end of the experiment (Table 2 and Figures 5b and 5e). That this particulate material was tiny aggregates (as opposed to only biominerals that had been added to the tanks) is shown by the fact that it contains both PIM and POM (Table 2).

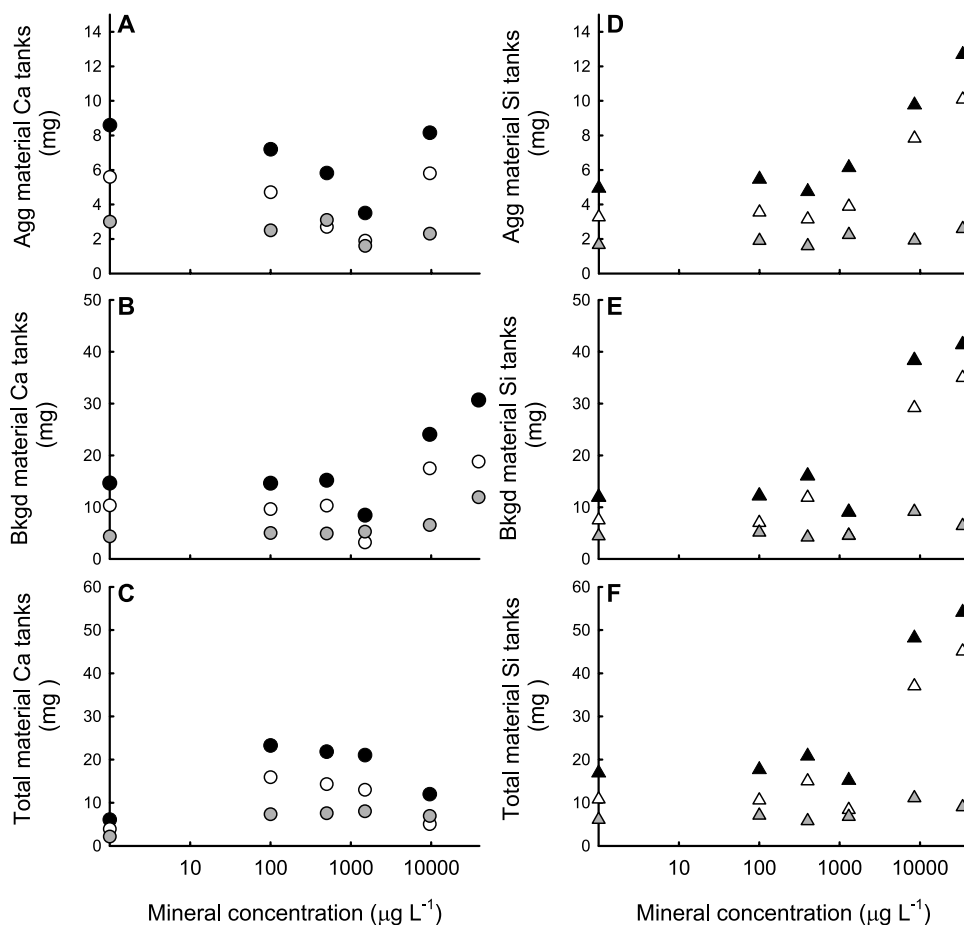
[20] The POC to dry weight ratio of these tiny aggregates, like that of large aggregates, is lowest in the tanks containing the greatest addition of minerals and approached an asymptote suggestive of saturation of the organic matter for adsorbing minerals (Figure 4). Whereas the large aggregates attained a final POC to dry weight ratio of about 5%, the tiny aggregates reached a slightly lower value of 2%. Quite significantly, there is no difference between the calcium carbonate experiment and the silica experiment, suggesting that there is no difference in the overall capacity of organic matter to retain calcium carbonate versus silica. This further underscores the point that organic matter can quite effectively scavenge suspended mineral particles from the water column and with them form aggregates [Passow and De La Rocha, 2006].

[21] If the difference between 5 weight % POC of large aggregates and 2 weight % POC for the tiny aggregates is significant, it is difficult to explain. If the minerals incorporated into the tiny aggregates are smaller, on average, than those scavenged into the large aggregates, then the POC to dry weight ratio of the tiny aggregates should be greater than that of the large aggregates. This is because the greater surface to volume ratio of the smaller particles mean that they should also have less mass per surface area. Thus if the saturation of the organic matter for retaining PIM is a function of surface area, the tiny aggregates would gain less mass for the same amount of mineral surface area retained (and would thus have a higher POC to dry weight ratio).

**Table 2.** Total Amount and Composition of the Particulate Material (i.e., Tiny Aggregates) Suspended in the Backgroundwater of the Rolling Tanks at the End of the Experiment<sup>a</sup>

Ca Tank	Initial [CaCO <sub>3</sub> ] ( $\mu\text{g L}^{-1}$ )	BKGD DW (mg)	BKGD POM (mg)	BKGD PIM (mg)	BKGD POM (%)	BKGD PIM (%)
1	0	14.7	4.3	10.3	29	71
2	100	14.6	5.0	9.6	34	66
3	500	15.2	4.9	10.3	32	68
4	1,500	8.4	5.3	3.2	62	38
5	9,600	24.1	6.6	17.5	27	73
6	39,000	30.7	11.9	18.8	39	61
Si Tank	Initial [SiO <sub>2</sub> ] ( $\mu\text{g L}^{-1}$ )	BKGD DW (mg)	BKGD POM (mg)	BKGD PIM (mg)	BKGD POM (%)	BKGD PIM (%)
1	0	11.9	4.4	7.5	37	63
2	100	12.2	5.2	7.0	42	58
3	400	16.1	4.2	11.9	26	74
4	1,300	9.0	4.5	4.5	50	50
5	8,500	38.4	9.2	29.2	24	76
6	34,000	41.4	6.4	35.0	15	85

<sup>a</sup>BKGD stands for backgroundwater.



**Figure 5.** Particulate material, PIM, and POM in aggregates, the backgroundwater, and total in experimental tanks. (a–c) The calcium carbonate tanks and (d–f) the results for the silica tanks. Figures 5a and 5d show the mg of PIM (open symbols), POM (gray symbols), and total particulate material (black symbols) in large aggregates. Figures 5b and 5e show the mg of PIM (open symbols), POM (gray symbols), and total particulate material (black symbols) in the backgroundwater. Figures 5c and 5f show the total (i.e., aggregate plus background) mg of PIM (open symbols), POM (gray symbols), and total particulate material (black symbols) present in each of the tanks.

### 3.3. PIM and POM Budgets

[22] The aggregates inoculated into the rolling tanks at the beginning of the calcium carbonate and silica experiments (which were run in parallel) contained an average 65 wt % PIM and 35 wt % POM. Although there was undoubtedly variability in the total mass of the 11 aggregates that were added to each rolling tank, on average they should have contained 5.4 mg of dry weight, 3.5 mg of which was PIM and 1.9 mg of which was POM.

[23] At the end of the experiment, the total dry weight of material present as aggregates larger than 1 mm (Table 3 and Figures 5a and 5d) often exceeded the 5 mg of dry weight that had been added as aggregates at the beginning of the experiment. In some cases this was possibly due to the addition of a larger than average amount of aggregate at the beginning of the experiment (e.g., calcium carbonate Tanks 1 and 2). In the rest of the tanks showing excessive amounts of aggregate dry weight, the increase resulted from the addition of PIM to the aggregates (Table 3 and

Figures 5a and 5d). In these cases, enough suspended minerals had been added to the tanks for the addition of PIM to be entirely due to the adsorption of the suspended minerals (Table 1).

[24] When the particulate material in the large aggregates is considered together with that of the tiny aggregates, it becomes evident that many (if not all) of the tanks contained more particulate material at the end of the experiment than had been added at the beginning (Table 4 and Figures 5c and 5f). For example, in calcium carbonate Tanks 1–3 and in silica tanks 1–4, the total dry weight of large and tiny aggregates is 1.3 to 4.3 times more than what had been initially added as aggregates and biominerals (Table 4). For Tanks 1–3, the subtraction of the amount of dry weight added from the amount of dry weight recovered gives an average excess dry weight at the end of the experiment of  $14.3 \pm 2.7$  mg per tank.

[25] It is likely that there was also excess material in Tanks 5 and 6. The undersampling of the particulate material in these tanks (Table 4) suggests that some partic-

**Table 3.** Total Amount and Composition of the Aggregates Greater Than 1 mm in Size at the End of the Experiment<sup>a</sup>

Ca Tank	Initial [CaCO <sub>3</sub> ] ( $\mu\text{g L}^{-1}$ )	AGG DW (mg)	AGG POM (mg)	AGG PIM (mg)	AGG POM (%)	AGG PIM (%)
1	0	8.6	3.0	5.6	35	65
2	100	7.2	2.5	4.7	35	65
3	500	5.8	3.1	2.7	53	47
4	1,500	3.5	1.6	1.9	46	54
5	9,600	8.2	2.3	5.9	28	72
6	39,000	–	–	–	–	–

Si Tank	Initial [SiO <sub>2</sub> ] ( $\mu\text{g L}^{-1}$ )	AGG DW (mg)	AGG POM (mg)	AGG PIM (mg)	AGG POM (%)	AGG PIM (%)
1	0	4.9	1.7	3.3	34	66
2	100	5.5	1.9	3.6	35	65
3	400	4.8	1.6	3.1	34	66
4	1,300	6.1	2.2	3.9	36	64
5	8,500	9.8	1.9	7.8	20	80
6	34,000	12.7	2.6	10.1	20	80

<sup>a</sup>AGG stands for aggregate.

ulates too small to be seen settled to the bottom of the tanks before the sampling of the backgroundwater and thus escaped measurement. And, despite this apparent under-sampling of the total particulate material, more POM was recovered than had initially been introduced into the tanks as aggregates. The amount of POM recovered in large aggregates and as tiny aggregates in the backgroundwater of Tanks 5 and 6 (or in the case of calcium carbonate Tank 6, the backgroundwater alone) ranged from 8.9 to 11.9 mg, well in excess of the approximately 2 mg introduced with the aggregates at the beginning of the experiment.

### 3.4. Origin of the Excess Particulate Matter

[26] The appearance of an extra 14 mg of particulate material in the rolling tanks (or roughly 3 mg per L) requires some explanation. The excess material consisted of both PIM and POM (Table 4 and Figure 5), requiring somehow that both organic and inorganic matter shifted from existing in a dissolved size class (i.e., small enough to pass through filters) to being large enough to be collected on a GFF filter. One explanation is that new POM was formed through coagulation of dissolved organic matter (DOM) present in the filtered seawater used in the experiments. The increase in the PIM would then either reflect the association of ions (like Ca<sup>2+</sup> and K<sup>+</sup>) with the organic polymers or would be related to the incorporation into the organic matter of tiny minerals that were somehow present in the filtered seawater.

[27] The shifting of DOM into the particulate phase is a process whose occurrence has been long since recognized [Riley 1963; Sheldon *et al.*, 1967; Johnson and Cooke, 1980; Allredge *et al.*, 1993; Chin *et al.*, 1998; Verdugo *et al.*, 2004]. Seawater that is filtered of its particles has been seen to immediately begin reforming particulate material via the assembly of gels from DOM and polymers. In terms of the experiment here, seawater is known to contain 0.5 to 2.4 mg L<sup>-1</sup> high molecular weight DOC [Eglinton and Repeta, 2003]. This is more than enough to have supplied the 2 mg of additional POM that formed during the experiment.

[28] One interesting question is the role of the minerals in this shifting of DOM into the particulate phase. The removal of significant quantities of DOM from solution through its adsorption onto minerals has been observed in estuaries [Uher *et al.*, 2001], rivers [Aufdenkampe *et al.*, 2007], sediments [Arnarson and Keil, 2000] and soils [Guggenberger and Kaiser, 2003]. Adsorption of minerals also is known to stabilize the structure of aggregates of POC [Kovac *et al.*, 2004]. In addition, large amounts of particulate material containing both PIM and POM have been seen to form in series of rolling tanks containing nothing but filtered seawater and suspensions of clay (M. Robert, personal communication, 2007). In the experiments reported here, the excess 8.9 to 11.9 mg of POM in Tanks 5 and 6 in both experiments is 4 to 7 mg greater than the average POM excess of 5 mg in Tanks 1–3, implying that more POM formed from DOM in tanks with a higher content of minerals. This is a result that needs to be looked at in more detail in future experiments as the scavenging of DOM into the particulate phase by minerals (and other particles) represents a pathway, in addition to the microbial loop, by which DOC could reenter the biological pump and sink to depth.

[29] One curious aspect of the excess particulate material is that, from the LOI data, it appears to consist not only of organic matter but of inorganic material as well. There are only 2 ways to explain such a result. The first is that there was a significant amount of minerals less than 0.2  $\mu\text{m}$  present in the filtered seawater used in the experiments. The second is that the bulk of the dry weight of the formed POM comes from ions helping to stabilize its structure.

[30] The seawater in the experiments was collected in the North Sea and was filtered through a 0.2  $\mu\text{m}$  cartridge filter prior to use. The North Sea is fairly shallow, is rimmed in part by mudflats, and receives a significant amount of runoff from the European continent. As a result, it can be

**Table 4.** Sum and Composition of the Particulate Material Present in Large Aggregates and Background at the End of the Experiment Compared to the Addition of Aggregates and Minerals at the Beginning<sup>a</sup>

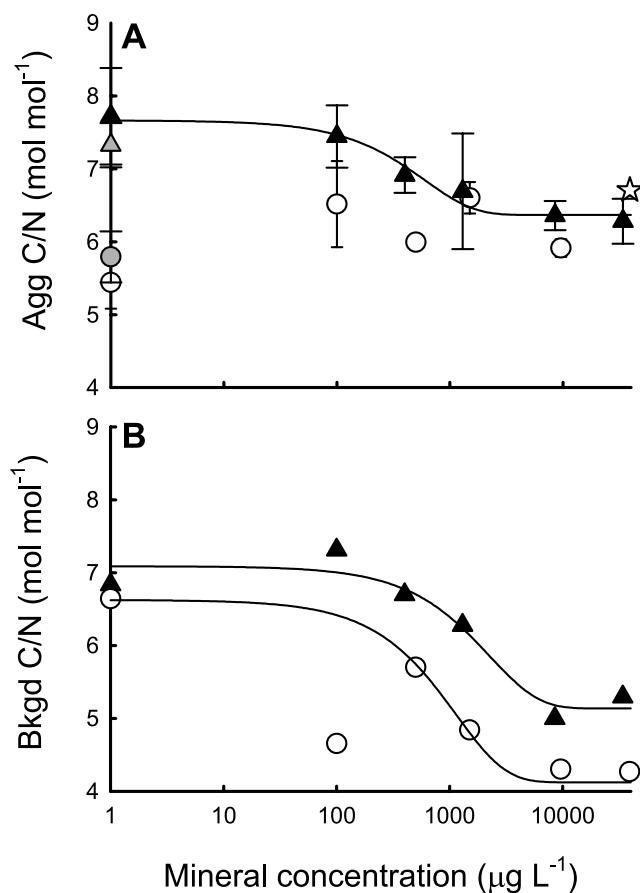
Ca Tank	Initial [CaCO <sub>3</sub> ] ( $\mu\text{g L}^{-1}$ )	Total DW Added (mg)	Total DW at End (mg)	Total POM at End (mg)	Total PIM at End (mg)
1	0	5.4	23.2	7.3	15.9
2	100	5.8	21.8	7.5	14.3
3	500	7.4	21.0	8.0	13.0
4	1,500	12.4	11.9	6.9	5.0
5	9,600	48.4	32.2	8.9	23.3
6	39,000	181.4	–	–	–

Si Tank	Initial [SiO <sub>2</sub> ] ( $\mu\text{g L}^{-1}$ )	Total DW Added (mg)	Total DW at End (mg)	Total POM at End (mg)	Total PIM at End (mg)
1	0	5.4	16.9	6.1	10.8
2	100	5.8	17.6	7.1	10.6
3	400	7.4	20.8	5.8	15.0
4	1,300	11.4	15.2	6.8	8.4
5	8,500	43.4	48.1	11.1	37.0
6	34,000	158.4	54.1	9.0	45.1

<sup>a</sup>On the basis of an average aggregate addition of 5.4 mg of dry weight.





**Figure 6.** C to N ratios of (a) macroscopic aggregates and (b) miniscule aggregates suspended in the backgroundwater at the end of the experiments. Symbols are as in Figure 3. The curve fit through the opal data in Figure 6a is  $y = 6.37 + 1.30e^{0.00167x}$  ( $r^2 = 0.97$ ). The curve fit through the opal data in Figure 6b is  $y = 5.14 + 195e^{0.00040x}$  ( $r^2 = 0.95$ ). The curve fit through the calcium carbonate data in Figure 6b (ignoring the point at  $100 \mu\text{g L}^{-1}$ ) is  $y = 4.12 + 2.50e^{0.00087x}$  ( $r^2 = 0.97$ ).

extremely turbid, containing up to  $70 \text{ mg L}^{-1}$  of particles [Ferrari *et al.*, 2003], many of which will be clays and other minerals. Clay can exist in the  $<0.2 \mu\text{m}$  size fraction, and it does not seem like too much of a stretch for there to have been at least  $3 \text{ mg L}^{-1}$  of dissolved clay present in the filtered seawater used in this experiment. Three  $\text{mg L}^{-1}$  of dissolved clay, scavenged into a larger size fraction during the experiment would be enough to account for the excess PIM found in Tanks 1–3.

[31] There are, however, good arguments for assigning at least some of the extra weight to ions cross-linking the organic matter. Cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are known to stabilize organic polymers [Verdugo, 1993]. In addition, the formation of calcium mineral polymers has been seen in spontaneously assembling marine gels [Chin *et al.*, 1998]. Prefiguring the ballast hypothesis, [Chin *et al.*, 1998] postulated that such calcite could increase the sinking velocities of aggregates formed in this manner. If significant amounts of calcite do form within spontaneously assem-

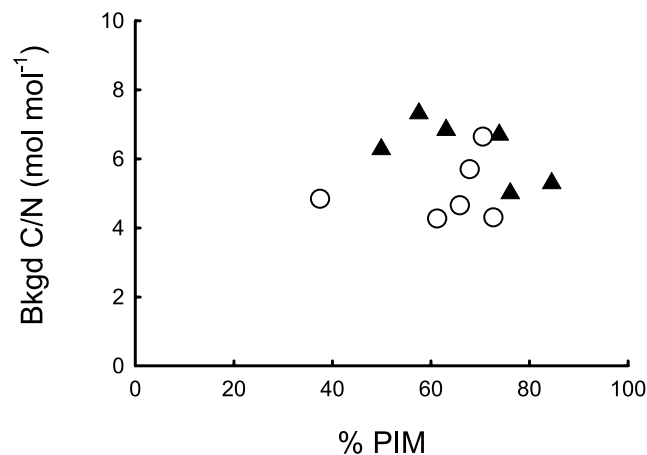
bling organic aggregates, they could be contributing to the strong correlation observed between calcium carbonate and POC fluxes into the deep sea.

### 3.5. Decline of the C to N Ratios

[32] The other impact that minerals appear to have had is on the C to N ratio of the particulate material. Although there was no clear decrease in the C to N ratio of the large aggregates in the calcium carbonate experiment, the C to N ratio of the large aggregates in the silica experiment dropped exponentially from  $7.7 \text{ mol mol}^{-1}$  in Tank 1 to  $6.3 \text{ mol mol}^{-1}$  in Tank 6 (Figure 6a), with the bulk of the change occurring between Tanks 2 and 4. Even more marked was the decrease in the C to N ratio of the tiny, suspended aggregates which formed in the backgroundwater in both experiments (Figure 6b). In the calcium carbonate experiment, the C to N ratios of this background particulate material dropped from  $6.6$  to  $4.3 \text{ mol mol}^{-1}$  between Tanks 1 and 6 and in the opal experiment it dropped from  $6.8$  to  $5.0 \text{ mol mol}^{-1}$ . In addition to the differences in C to N ratios between the macroscopic aggregates and those tiny aggregates formed from DOM and tiny suspended minerals, C to N ratios from the calcium carbonate tanks were lower than those from the corresponding opal tanks (Figure 6b).

[33] There are several possible explanations for the decline in C to N ratios with increasing concentration of added minerals. The patterns could be analytical in nature, resulting from some interference to the C to N analysis due to the presence of calcium carbonate or silica. Alternatively, the trends could be associated with the C to N ratio of organic compounds scavenged out of the DOM pool, or they could be linked to changes in the C to N ratio during the decomposition of organic matter.

[34] The observed trends in C to N ratios are probably not artifacts of the analysis because C to N ratios showed no relationship to the PIM content of the material analyzed (Figure 7). The linear correlation between PIM and C to N ratio was not significant for the opal tanks ( $y = -0.046x +$



**Figure 7.** C to N ratio of particulate matter in the background water in the tanks at the end of the experiment versus the PIM content of this material. Symbols are as in Figure 3.

9.31;  $r^2 = 0.41$ ;  $n = 6$ ;  $p > 0.05$ ) alone, the calcium carbonate tanks alone ( $y = 0.02x + 4.01$ ;  $r^2 = 0.07$ ;  $n = 5$ ;  $p > 0.05$ ), nor all the tanks taken together ( $y = -0.004x + 5.9$ ;  $r^2 = 0.002$ ;  $n = 12$ ;  $p > 0.05$ ).

[35] It is also unlikely that differential rates of remineralization of C and N from organic matter was responsible for the lower C to N ratios in tanks with more minerals. Faster rates of bacterial degradation of PON than POC, for example, generally result in detritus with a high C to N ratio [Verity *et al.*, 2000]. Likewise, the C to N ratio of particles, sinking and decomposing in the ocean, increases with depth up to 11 mol mol<sup>-1</sup> by a depth of 5 km [Martin *et al.*, 1987].

[36] It may instead be that some organic compounds bind more easily or more strongly to minerals than others, resulting in the differential scavenging of organic compounds (for example, amino acids versus carbohydrates) and thus relative accumulation of POC and PON. For example, the data on data Figure 6b could indicate that the C to N ratio of POM scavenged out of the DOM pool through interaction with dissolved inorganic material present in the filtered seawater was around 6.7 mol mol<sup>-1</sup>. But the C to N ratios of DOM scavenged by opal and calcium carbonate were, respectively, closer to 5 mol mol<sup>-1</sup> and 4 mol mol<sup>-1</sup>. The drop in the C to N ratios of the background particulate material in Tanks 2–5 would then represent the increased proportion of POM produced from DOM by the added biominerals. The smaller decline in the C to N ratio of macroscopic aggregates (Figure 6a) would represent the same process, suggesting that the macroscopic diatom aggregates also scavenged DOM out of the water.

### 3.6. Implications for the Ballast Hypothesis

[37] In its original form, the ballast hypothesis, based on correlations between POC and mineral fluxes into sediment traps in the deep ocean, suggests that fluxes of POC to the deep sea may be determined by the flux of minerals, and that calcium carbonate is a more efficient “carrier” of POC than biogenic silica [Armstrong *et al.*, 2001; François *et al.*, 2002; Klaas and Archer, 2002]. The validity of drawing such conclusions from correlations has been questioned [Passow 2004; Passow and De La Rocha, 2006; De La Rocha and Passow, 2007] and it is clear that work needs to be done to quantify the processes by which POC and mineral fluxes are linked. From the resulting mechanistic understanding of the fluxes, perhaps then models of POC export can be improved.

[38] The results of this experiment have several implications for the ballast hypothesis. The first is that they yielded no evidence that calcium carbonate has a higher carrying capacity for organic matter than opal does. In rolling tank experiments with aggregates and minerals reported here and in [Passow and De La Rocha, 2006], the dry weight to POC ratio of aggregates saturated at essentially the same level of 2–5 weight percent POC (Figure 4) [Passow and De La Rocha, 2006, Figure 4]. This occurred regardless of whether the mineral was reagent grade calcium carbonate, biogenic calcium carbonate, clay (illite), or biogenic opal and whether the aggregates were initially formed in the absence of suspended minerals, were fragmented off of larger aggre-

gates, or were formed by the scavenging of DOM onto tiny mineral particles.

[39] The reproducibility of the saturating POC to dry weight ratio of the different aggregates and its correspondence to the 5 weight percent POC of fluxes into deep sediment traps [Armstrong *et al.*, 2001] strongly implies that this is a general feature of organic matter-mineral interactions in seawater. It also implies that it is incorrect to interpret the “carrying coefficients” that fall out of the multiple regression analysis [Klaas and Archer, 2002] as indicating anything about the physical strength of the association between POC and various different minerals. Thus while the calculated “carrying coefficients” might describe the relationships between POC and mineral fluxes in the modern ocean, it is possible that they are reflecting the relative variability in fluxes of POC versus the various different minerals (calcium carbonate, biogenic silica, and lithogenic silica). For example, the POC to biogenic silica ratio of sinking fluxes is strongly related to the diatom contribution to primary production in different regions (with the lowest ratios occurring at the highest levels of silica production) [Ragueneau *et al.*, 2000] and may be indicating nothing about the efficiency of biogenic silica to pick up and carry POC to depth.

[40] Another implication for the ballast hypothesis is the observation of the formation from DOM of tiny aggregates, too small to be seen or to settle with any appreciable velocity and containing both PIM and POM. Further coagulation of these minuscule aggregates into larger ones or their incorporation into aggregates already large enough to sink could provide a pathway for the export of previously dissolved organic matter to the deep sea and sediments. These results are important to the ballast hypothesis regardless of whether this PIM was cations like Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> cross-linking the organic polymer formed and helping to stabilize it [Verdugo *et al.*, 2004], whether it was calcium-minerals formed within the organic matter matrix [Chin *et al.*, 1998], or whether this PIM represented suspended clay minerals that passed through the 0.2 μm pre-filtration of the seawater used in the experiment. Given that the mass of minuscule aggregates formed in the experiments here was sizable (i.e., in all cases greater than the mass of the 11 large aggregates inoculated into each rolling tank), this pathway could be making a significant contribution to POC flux from the surface ocean. In addition, these results strongly support the idea that organic matter acts as the “glue” allowing POC-mineral association possible [Armstrong *et al.*, 2001], and they could also go some way toward explaining the homogeneity of the dry weight to POC ratios of sinking fluxes in the deep ocean [Armstrong *et al.*, 2001; François *et al.*, 2002; Klaas and Archer, 2002].

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