

Accumulation of mineral ballast on organic aggregates

Uta Passow, Christina De La Rocha

► **To cite this version:**

Uta Passow, Christina De La Rocha. Accumulation of mineral ballast on organic aggregates. Global Biogeochemical Cycles, American Geophysical Union, 2006, 20 (1), pp.GB1013. <10.1029/2005GB002579>. <hal-00467271>

HAL Id: hal-00467271

<http://hal.univ-brest.fr/hal-00467271>

Submitted on 12 Aug 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accumulation of mineral ballast on organic aggregates

Uta Passow¹ and Christina L. De La Rocha¹

Received 24 June 2005; revised 11 October 2005; accepted 4 January 2006; published 28 February 2006.

[1] To address whether the incorporation of suspended minerals drives the sedimentation of particulate organic carbon in the ocean or vice versa, incubations of phytoplankton-detritus aggregates were set up in rolling tanks containing seawater and suspended clay (illite) or calcium carbonate at concentrations ranging between 10 and 50,000 $\mu\text{g L}^{-1}$. The suspended minerals were efficiently scavenged by and incorporated into the organic aggregates. The volume and porosity of aggregates decreased with increasing mineral concentrations, and at suspended mineral concentrations higher than 500 $\mu\text{g L}^{-1}$ the initially medium-sized aggregates were fragmented into thousands of tiny, dense aggregates. Because radius and density have opposite effects on aggregate sinking rates, the relationship between aggregate particulate organic carbon (POC) to mineral ratio and sinking rate is not a straightforward one that necessarily results in higher sinking rates with increased mineral content. In these experiments the saturating capacity of organic aggregates for mineral particles appeared to be 97 to 98 weight-percent mineral (i.e., a POC to dry weight ratio of 0.02 to 0.03 $\mu\text{g C } \mu\text{g}^{-1}$). This parallels the values of 0.05 $\mu\text{g C } \mu\text{g}^{-1}$ observed for sinking particles in the deep sea and suggests that it is the flux of POC that determines the flux of minerals to the deep and not the other way around.

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

1. Introduction

[2] The accumulation of organic carbon in marine sediments is a key sink of carbon from the ocean-atmosphere system. Only 1% [Sundquist, 1993] of the yearly 50–60 Pg C of marine primary production [Field *et al.*, 1998] survives sinking through the water column to reach the seabed, making the processes that occur during sinking key to the efficiency of the biological pump. The large regional variability in sinking POC fluxes observed in the upper ocean, but not seen below 3000 m [Antia *et al.*, 2001], suggests that processes important in the mesopelagic and bathypelagic zones (such as fragmentation, aggregation, degradation, solubilization, dissolution, grazing or scavenging) have a significant impact on POC flux.

[3] The aggregation of particulate organic carbon (POC) into particles large enough to attain high sinking rates given the viscous constraints of seawater on small particles is critical to the sedimentation of POC [McCave, 1975; Billett *et al.*, 1983]. The accumulation of “ballast minerals” such as clays, calcium carbonate, and silica on organic aggregates may affect the aggregation, sinking velocity, and flux of POC [Ittekkot, 1993; Armstrong *et al.*, 2002; François *et al.*, 2002; Hamm, 2002; Klaas and Archer,

2002]. Ballast minerals have been postulated to enhance the fraction of surface primary production that reaches the seabed by either protecting the organic matter from oxidation or increasing the density, and thus the sinking rate, of organic aggregates. In response to the recent works of Armstrong *et al.* [2002], François *et al.* [2002], and Klaas and Archer [2002], the idea that such mineral ballasting controls the amount of particulate organic carbon reaching the deep sea is causing a shift in the way the biological pump is considered and modeled [e.g., Barker *et al.*, 2003; Ridgwell, 2003; Heinze, 2004]. Given the significance of that, the ballast hypothesis needs to be examined in more detail.

[4] Although minerals have long been known to enhance the flocculation of phytoplankton aggregates [Avnimelech *et al.*, 1982], there have been few direct observations of the interactions between minerals and organic aggregates. Recent experiments have shown that the aggregation of diatom cells is enhanced by high concentrations of clay minerals [Hamm, 2002]. In this experiment, the concentration and type of mineral present had an influence on the character (e.g., size and porosity) of the aggregates that formed, which meant that there was no straightforward relationship between sinking rates and the accumulation of minerals into the aggregates.

[5] In the deep sea the sinking fluxes of organic matter and of minerals are related [Armstrong *et al.*, 2002; François *et al.*, 2002; Klaas and Archer, 2002]. Below 3000 m, sinking particles contain a fairly constant 5 weight percent of organic carbon [Armstrong *et al.*, 2002]. The flux

¹Alfred-Wegener-Institut für Polar und Meeresforschung, Bremerhaven, Germany.

of calcium carbonate into sediment traps below 3000 m also appears to correlate (r^2 values around 0.7) with the flux of POC into these traps [François *et al.*, 2002; Klaas and Archer, 2002]. The correlation between opal fluxes and POC fluxes is not as strong but is still significant [François *et al.*, 2002; Klaas and Archer, 2002]. The major conclusions that have been drawn from these correlations are that organic matter sinking in the sea is “carried” down by such mineral “ballast” [Armstrong *et al.*, 2002], and that the primary mineral responsible for the sedimentation of POC is calcium carbonate [François *et al.*, 2002; Klaas and Archer, 2002].

[6] Unfortunately, the regression analyses overlook the fact that Si: C ratios of primary production vary greatly from region to region, for example, $0.1 \text{ mol Si (mol C)}^{-1}$ in the Atlantic versus $3.3 \text{ mol Si (mol C)}^{-1}$ in the North Pacific [Ragueneau *et al.*, 2000, Figure 5]. Areas of high organic matter flux are characterized by high Si: C ratios because a high fraction of the export production is carried out by diatoms [Ragueneau *et al.*, 2000]. Thus, although diatoms are producing most of the export production, the resulting high ratio between Si: C erroneously suggests a low efficiency of opal as a transport vehicle. And, the variability in the Si: C production ratio translates into the low correlation coefficients in the global sediment trap data set that have led to the inaccurate conclusion that opal is unimportant for organic matter flux into the deep sea.

[7] Another reason why regressions may not be the best way of looking at sediment trap data is that correlation does not imply causation. There is no information to suggest that it is the mineral fluxes driving the organic ones; it could just as easily be the other way around. Historically, the opposite conclusion, that sinking POC is responsible for the sedimentation of mineral particles, has been drawn [e.g., Deuser *et al.*, 1983].

[8] When the sediment trap data are considered from the viewpoint that it is aggregates of POC that scavenge suspended minerals as they sink, the data suggest that sinking aggregates will scavenge mineral particles until the aggregates are “saturated” at 95 weight-% mineral [Passow, 2004]. This in turn suggests the existence of a pool of small ($<5 \mu\text{m}$), negligibly sinking particles (such as clays, coccoliths, and fragments of diatoms, foraminifera, and radiolarians), in the mesopelagic and bathypelagic zones. Concentrations of such non-sinking particles, which in the absence of aggregates that transport them to depth, would dissolve (coccoliths or opal) or accumulate (clays) in the mesopelagic and bathypelagic zones await quantification. To explain the tighter correlation between calcium carbonate and POC than between opal and POC in sediment trap data [Klaas and Archer, 2002], this suspended mineral pool would have to be dominated by coccoliths, and be too low in opal to overprint the variability in the Si: C ratio of aggregates from the surface ocean. Alternatively, the pick-up of suspended opal by sinking aggregates might be sufficiently inhibited by the low binding efficiency of the polysaccharide matrix of sinking aggregates for opal [Moulin and Moulin, 2001; Moulin *et al.*, 2004].

[9] To test at what point organic aggregates reach their capacity for binding minerals [Passow, 2004], we simulated

the sinking of mixed diatom and fecal pellet aggregates in rolling tanks containing different concentrations of calcium carbonate and the clay, illite. Herein we report the effects of the mineral scavenging on aggregate size and number, and of the scavenging ability of organic aggregates for mineral particles.

2. Methods

[10] Organic aggregates were generated from 8 L of a dense culture of *Thalassiosira weissflogii* to which had been added 0.15 g of dried *T. weissflogii* and 6 mL of dense detritus (feces, eggs, molts) from cultures of the copepods *Tenora* sp. and *Acartia tonsa*. The copepod detritus was frozen prior to use to kill eggs and nauplii. The diatom-detrital mix was incubated at low light for 2–7 days in 8-L cylindrical tanks on roller tables [Shanks and Edmondson, 1989] before the harvesting of the aggregates that formed through collisions of particles settling at different rates through the rotating medium [Jackson, 1994]. Resulting aggregates consisted of a mixture of live and dead diatoms, fecal pellets and miscellaneous, unidentifiable organic matter and thus reflected the composition of natural marine aggregates [Allredge and Gotschalk, 1990; Silver and Allredge, 1981].

[11] Concentrated solutions of illite and calcium carbonate (Sigma, analytical grade) were prepared. The illite had a specific surface area of $94.4 \text{ m}^2 \text{ g}^{-1}$ and a cation exchange capacity of $0.2\text{--}0.5 \text{ meq g}^{-1}$ dry weight [Hamm, 2002]. The calcium carbonate was not similarly characterized. The solutions were placed in a settling column and only that material settling more slowly than 4 cm h^{-1} was siphoned off, brought up to a final volume of 1.5 g L^{-1} illite or 0.75 g L^{-1} calcium carbonate in 35 g L^{-1} NaCl, and used in the experiment.

[12] At the onset of the experiment, seven 2-L cylindrical acrylic tanks were filled with 1.5 or 1.9 L of $0.2 \mu\text{m}$ filtered seawater amended with $30 \mu\text{M}$ silicic acid, $15 \mu\text{M}$ nitrate, and $1 \mu\text{M}$ phosphate (to simulate deep water conditions). Between 0.013 and 133 mL of the concentrated illite or calcium carbonate solution was added to each tank to produce a range of suspended mineral concentrations from 7 to $50,000 \mu\text{g L}^{-1}$ (Table 1). Five to six selected aggregates were transferred intact into each tank. The tanks were then gently topped off with nutrient-amended seawater introduced slowly through a syringe. The tanks were then closed and placed on the roller table and rolled at 0.43 RPM in darkness for 2 days.

[13] The 5–6 aggregates of similar size inoculated into each tank were selected from a set of 80–100 harvested from the 8-L cylindrical tanks. The 80–100 aggregates were isolated individually by being mouth-pipetted into a disposable 10-mL plastic pipette whose tapered end had been cut off. Each aggregate was then transferred into a Petri dish filled with filtered seawater. Aggregates that came apart during this process were discarded. Aggregates were then immediately sized (length versus width) against mm quadrilled paper with the aid of a binocular microscope. Five to six intact aggregates of the same size were selected at random and placed in each of the seven tanks or set aside

as one of the four replicate sets of aggregates used to determine the composition of aggregates at time zero.

[14] After 48 hours, the number of aggregates in each tank were counted and described. Aggregates large enough to be collected (>1 mm) were sized and then collected on pre-weighed silver filters for measurement of their dry weight and POC content. Filters were dried at 60°C for 2 hours prior to weighing on an electrobalance and analysis for POC content using an elemental analyzer (ANCA SL 20-20). Samples from the calcium carbonate ballast experiment were decarbonated with HCl before they were run through the elemental analyzer. The volumes of the aggregates were calculated for the aggregates as prolate spheroids,

$$V_{\text{agg}} = (4/3)\pi ab^2, \quad (1)$$

where a is half the width and b is half the length of the aggregate.

[15] Three or four times during each experiment, samples were also taken (while the tanks were rolling) of the background solution using a syringe stuck through a silicone stopper in the side of the tanks. Background concentrations of illite were measured as absorbance in a spectrophotometer using a wavelength of 275 nm, which was the peak absorbance found for suspensions of this material. A calibration curve between illite concentration (in mg L^{-1}) and absorbance at 275 nm ($[\text{illite}] = 0.006(\text{abs}_{275}) - 0.023$; $r^2 = 0.999$) was established using standard solutions of illite (plus $35 \text{ g kg}^{-1} \text{ NaCl}$) ranging from 2 to 100 mg L^{-1} . A similar approach did not work for the calcium carbonate solutions as the peak absorbance fell too close to that of dissolved organic carbon (DOC) to be utilized.

3. Results

[16] The amount of dry weight inoculated into each of the experimental tanks as aggregates was $2950 \pm 666 \mu\text{g}$ in the illite experiment and $2144 \pm 291 \mu\text{g}$ in the calcium carbonate experiment. The C content of one set of initial aggregates in the illite experiment was $369 \mu\text{g}$, yielding an initial POC to dry weight ratio of $0.17 \mu\text{g C } \mu\text{g}^{-1}$. The average POC content and POC to dry weight ratio of initial aggregates in the calcium carbonate experiment were $319 \pm 32 \mu\text{g C}$ and 0.15 ± 0.01 , respectively.

[17] Concentrations of freely suspended minerals in the rolling tanks decreased over time, as shown by the drop in suspended illite concentrations (Figure 1). The fraction of suspended illite that was scavenged also decreased as concentrations dropped. By hour 48, background concentrations of illite in tanks 7, 6, and 4 had dropped by 90%,

Table 1. Suspended Mineral Concentrations in the Tanks

Tank	Illite, $\mu\text{g L}^{-1}$	CaCO_3 , $\mu\text{g L}^{-1}$
1	10	7
2	50	40
3	100	...
4	500	400
5	2000	1500
6	10,000	7000
7	50,000	37,000

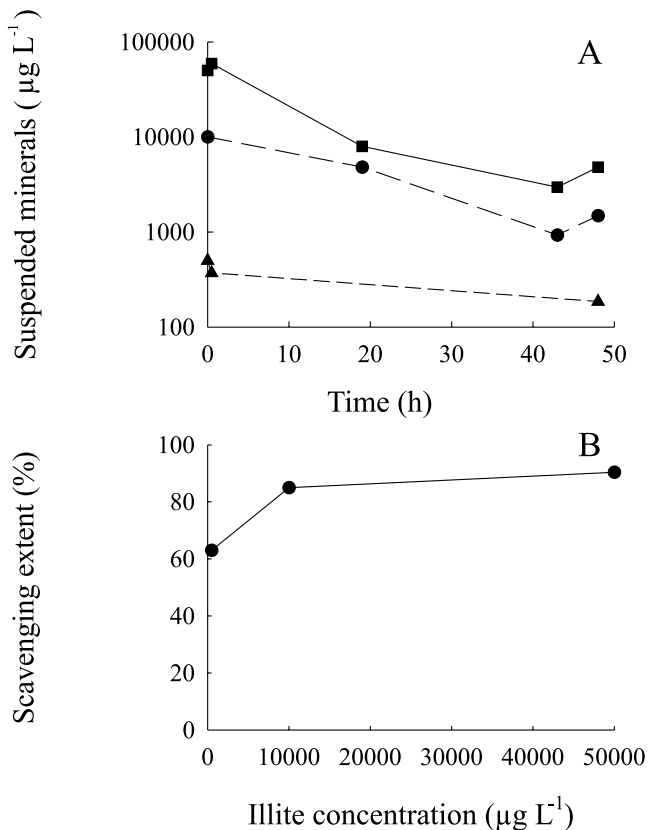


Figure 1. (a) Drop in the background concentration of suspended illite over time during the experiment in tank 4 (solid triangles), tank 6 (solid circles), and tank 7 (solid squares). (b) Percent of suspended illite scavenged by the end of the experiment.

85%, and 63%, respectively. Background concentrations in tanks 1–3 were below the detection limit.

[18] After 48 hours, the number of aggregates present in tanks 1–5 (i.e., suspended mineral concentrations below $2000 \mu\text{g L}^{-1}$) was similar to the number inoculated into the tanks (Figure 2a). Aggregate numbers began to significantly increase in tank 6, reaching more than 1000 in number in tank 7. The aggregates also grew smaller as the suspended mineral concentration of the tanks increased (Figure 2b). Between tanks 1 and 6, the average volume of aggregates larger than 2 mm^3 dropped from 190 mm^3 to 30 mm^3 in the illite experiment and from 150 mm^3 to 4 mm^3 in the calcium carbonate experiment (Figure 2b). There were no aggregates greater than 2 mm^3 in volume in tank 7 in either experiment.

[19] The aggregates also changed in character with increasing concentrations of freely suspended minerals. Aggregates in tanks with low concentrations of suspended minerals were large, green, and fluffy (e.g., photo as auxiliary material¹), while the aggregates in the higher concentration tanks were small, compact, and white. The small, compact aggregates were denser than the fluffier aggregates, requiring greater suction for removal from the

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gb/2005GB002579>.

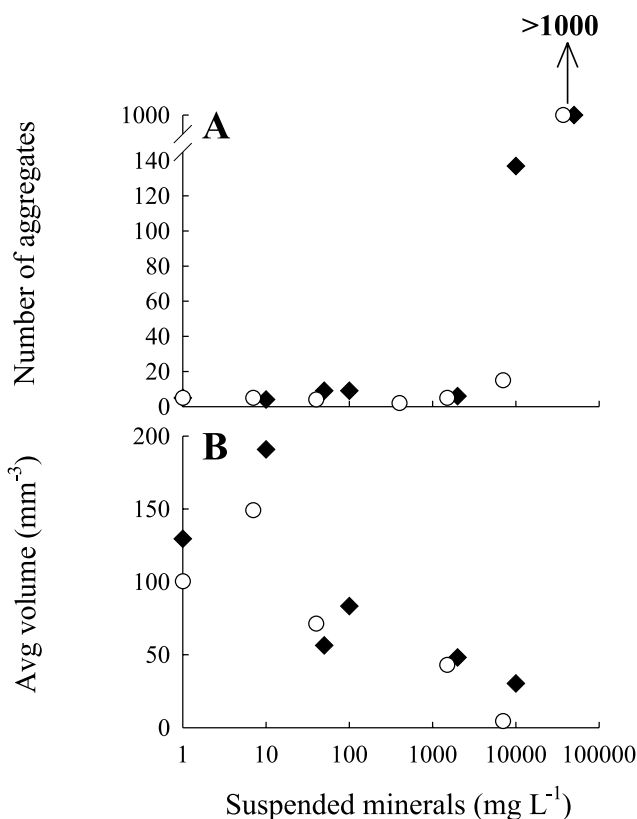


Figure 2. (a) Number of visible aggregates versus the concentration of suspended mineral particles in the illite (solid diamonds) and calcium carbonate (open circles) tanks. (b) Average volume of aggregates greater than 1 mm in length versus suspended mineral concentration in the illite (solid diamonds) and calcium carbonate (open circles) tanks. The number of aggregates at the highest concentration of suspended illite and calcium carbonate are both in excess of 1000.

tanks at the end of the experiment. In tank 7 in both experiments, the aggregates were too numerous, small, and dense to be quantitatively collected or accurately sized.

[20] The dry weight to volume ratio of aggregates in both experiments remained between 2.4 and 4.4 $\mu\text{g mm}^{-3}$ in tanks 1–4 (Figure 3). In the illite experiment they then increased to a plateau of $\sim 8 \mu\text{g mm}^{-3}$. In the calcium carbonate experiment, the dry weight to volume ratio of the aggregates shot up abruptly when suspended mineral concentrations rose above 500 $\mu\text{g L}^{-1}$ (Figure 3) and never showed signs of leveling off. These relationships can be described by the curves, $y = 2.44 + 5.78(1 - e^{-0.0008x})$, for the illite experiment ($r^2 = 0.91$) and $y = 2.64 + 0.0008x^{1.31}$, for the calcium carbonate experiment ($r^2 = 0.99$), where y is dry weight per volume and x is the initial suspended mineral concentration. The change in the dry weight to volume ratio at the higher calcium carbonate concentrations is greater than it is in the higher illite concentrations (Figure 3). No values could be calculated from tank 7 as the resulting multitude of tiny aggregates was too difficult to characterize.

[21] The aggregates in illite tanks 1–3 and calcium carbonate tanks 1–4 retained their initial POC to dry weight

ratio of $\sim 0.16 \mu\text{g C } \mu\text{g}^{-1}$ (Figure 4a). Above initial suspended mineral concentrations of 400 $\mu\text{g L}^{-1}$, there was an exponential decline (Figure 4a) in the POC to dry weight ratio of the aggregates in both the illite experiment ($y = 0.015 + 0.1320e^{-0.0002x}$; $r^2 = 0.97$) and the calcium carbonate experiment ($y = 0.033 + 0.1210e^{-0.0008x}$; $r^2 = 0.98$). By tank 7, POC to dry weight ratios settled at 0.015 $\mu\text{g C } \mu\text{g}^{-1}$ and 0.03 $\mu\text{g C } \mu\text{g}^{-1}$ in the illite and calcium carbonate experiments, respectively (Figure 4b).

4. Discussion

4.1. Concentrations of Suspended Minerals in the Rolling Tanks

[22] The purpose of these experiments was to study the incorporation of suspended minerals into organic aggregates as might occur as the aggregates sink through the ocean. Given the difference between the volume of a rolling tank and the ocean, it is worth considering how representative the rolling tanks are of marine conditions. The concentrations of illite and calcium carbonate used in these experiments ranged from 7 $\mu\text{g L}^{-1}$ to 50,000 $\mu\text{g L}^{-1}$ (Table 1). Particle concentrations in the ocean range from 0.5 to 250 $\mu\text{g L}^{-1}$, with the highest concentrations occurring in the surface and nepheloid layers and the lowest concentrations occurring at mid-depths [Biscaye and Eitrem, 1977; Simpson, 1982]. Concentrations of total suspended matter on the order of 70,000 $\mu\text{g L}^{-1}$ can occur in places like the North Sea [e.g., Ferrari et al., 2003]. Rolling tanks 1 through 3, covering 7 to 100 $\mu\text{g L}^{-1}$, are thus representative of general average particle concentrations found in the ocean. The suspended mineral concentrations of tanks numbered 4 through 7 (400 through 50,000 $\mu\text{g L}^{-1}$) are representative of more turbid systems, such as estuaries or the North Sea.

[23] The higher concentrations of freely suspended minerals were also useful in the experiment to simulate the

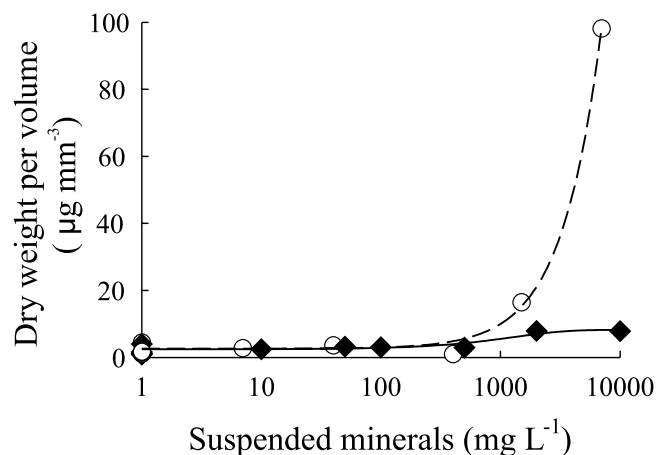


Figure 3. Dry weight to volume ratio of aggregates larger than 2 mm^3 in the illite experiment (solid diamonds) and calcium carbonate experiment (open circles) for different concentrations of suspended minerals. The curve fit to the illite experiment data (solid line) is $y = 2.44 + 5.78(1 - e^{-0.0008x})$, $r^2 = 0.91$. The curve fit to the calcium carbonate experiment data (dashed line) is $y = 2.64 + 0.0008x^{1.31}$, $r^2 = 0.997$.

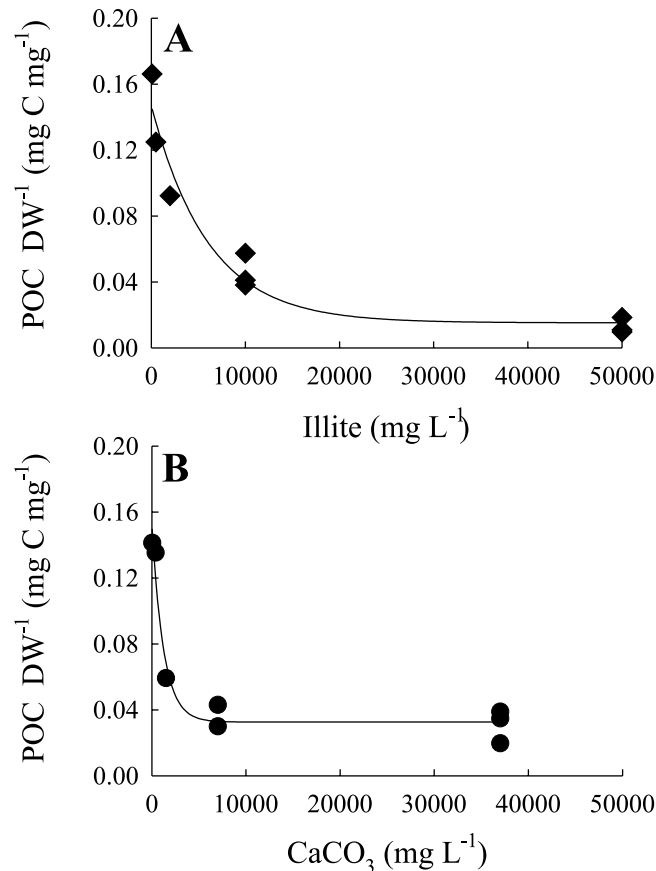


Figure 4. Decline in the POC to dry weight ratios versus the concentration of suspended mineral particles in the (a) illite and (b) calcium carbonate tanks. The curve fit to the data in Figure 4a is $y = 0.015 + 0.1320e^{-0.0002x}$ ($r^2 = 0.97$). The curve fit to the data in Figure 4b is $y = 0.033 + 0.1210e^{-0.0008x}$ ($r^2 = 0.98$).

number of particles aggregates might encounter as they sink several thousand meters. A spherical aggregate with a radius of 1 mm (and a volume of 3.1 mm³) will traverse a volume of 3.1 L for every 1000 m sunk. There were at least five aggregates inoculated into each experimental tank and their collective footprint averaged 1.8 cm². Such a collection of aggregates would sweep a volume of 180 L in 1000 m, and if they sunk 3000 m through a water column with an average particle concentration of 50 μg L⁻¹ [Simpson, 1982], they would encounter 27,000 μg of particulates. This is a rough estimate, but it is useful as a benchmark. 27,000 μg of particulate material is more than the amount of illite or carbonate in any of the tanks 1 through 6 (Table 1). Tank 7 contained a considerable excess of particulate matter above this number, and was used to ensure the production of aggregates “saturated” with ballast material.

4.2. Impact of Ballast on Aggregate Size, Character, and Number

[24] The adoption of the term, “ballast minerals,” for the clays, calcium carbonate, and silica observed to cosediment with POC gives the impression that minerals increase the sinking rates of POC by adding density to the particles [Armstrong *et al.*, 2002; François *et al.*, 2002; Klaas and

Archer, 2002]. This is a simple way of looking at the controls on particle sinking rates (W_{agg}), and it overlooks one point of Stoke’s Law, that sinking rates will also increase with the square of the radius of a particle,

$$W_{agg} = \frac{2}{9} \cdot \frac{g r_{agg}^2 (\Delta\rho)}{\mu}, \quad (2)$$

where g is acceleration due to gravity, μ is the dynamic viscosity of seawater, and $\Delta\rho$ is the density difference between the aggregate and seawater. That a drop in particle radius will diminish its sinking rate complicates the view of minerals as merely ballast; the illite and calcium carbonate experiments showed that the incorporation of minerals into organic aggregates can diminish aggregate size.

[25] In the experiments, there were three processes at work that would have had an impact on sinking rates. There was an increase in density of aggregates at high mineral concentrations due to the incorporation of minerals of relatively high specific gravity, as shown by the increase in dry weight to volume ratio of the aggregates at very high concentrations of suspended minerals (Figure 3). There was a drop in the volume of aggregates at low but increasing concentrations of suspended minerals (Figure 2b) that was

most likely due to a decline in the porosity of aggregates since it did not coincide with an increase in aggregate number (Figure 2a). Also, there was a drop in the volume of aggregates to below 2 mm^3 at high suspended mineral concentrations that was due to the fragmentation of the five initial aggregates into thousands of tiny ones (Figures 2a).

[26] This is not the first time such trends have been seen. Hamm [2002] also observed a decrease in aggregate volume and porosity with increasing suspended mineral concentration. His study also showed that both the composition of the aggregate, such as the dominant phytoplankton species making it up, and the type of suspended mineral present, have an impact on the shift in aggregate size and porosity. This also parallels results obtained here; although at low concentrations of suspended minerals the decrease in porosity of the aggregates was similar in both treatments, at higher concentrations, aggregates exposed to calcium carbonate had dry weight to volume ratios 2 to 10 times greater than those exposed to illite (Figure 3). Estimates of the porosity of natural aggregates also suggest that this value varies widely and increases with size [Allredge and Gotschalk, 1988, and references within].

[27] Although fragmentation and reduction in porosity both diminish the radii of aggregated materials, they have different contributions to the sinking rate of those aggregates. The reduction in radius, according to Stoke's Law will reduce the sinking rate of an aggregate; if fragmentation is the only process at work, the sinking rate should decline by the square of the radius (equation (2)). The effect of a reduction in porosity is more complicated. On the one hand it will result in an increase in the density of a particle, and thus its sinking rate. On the other hand it will also result in a drop in the radius of an aggregate, which will decrease the sinking rate of the aggregate. Whether or not the sinking rate increases will depend upon the balance struck between the reduction in the radius and the increase in density of the aggregate. These numerous effects of incorporated minerals on aggregate characteristics, and thus sinking rates, are why Hamm [2002] did not find that an increase in the mineral loading of an aggregate necessarily increased its sinking rate and may be why sinking rates in the deep sea do not seem to be strongly linked to the loading of particles with mineral ballast [Berelson, 2002].

4.3. Ballast Minerals as a Vehicle for POC Sedimentation or Vice Versa?

[28] If ballast minerals determine the flux of POC through the deep sea, the ballast minerals must be either controlling the sinking rates of POC or the percent of the POC that survives decomposition during its descent [Armstrong et al., 2002; François et al., 2002; Klaas and Archer, 2002]. As pointed out above and by Hamm [2002], the incorporation of minerals within aggregates does not necessarily increase their sinking rates. Also, there is no evidence for or against incorporated minerals providing protection from microbial degradation during sinking through the water column, although it has been postulated to occur over long time-scales in the sediments [Hedges and Keil, 1995].

[29] One alternative to the hypothesis of minerals driving the sedimentation of POC is that sinking aggregates of POC

drive the settling of minerals that would otherwise be too small to sink [Passow, 2004]. If this is the case, aggregates should be effective at scavenging suspended mineral particles from seawater. The aggregates in these experiments were quite effective at scavenging suspended ballast material. Five $\sim 600\text{-}\mu\text{g}$ aggregates removed 90% of the total $100,000 \mu\text{g}$ of illite inoculated into the 2 L of tank 7 in less than 48 hours (Figure 1). Although scavenging efficiencies were lower at lower illite concentrations, at the $500 \mu\text{g L}^{-1}$ of illite of tank 4, the aggregates picked up more than half of the suspended material within 48 hours. Given more time than this, these aggregates may have acquired an even larger fraction of the available suspended matter, as these aggregates in tank 4 were not saturated with respect to their ability to absorb ballast (Figure 4).

[30] The effectiveness of organic aggregates at scavenging suspended minerals is not surprising. Aggregates, especially diatom flocs, are laden with exopolymers which contribute to holding them together and also make them "sticky" [Allredge and Silver, 1988], increasing their chances to retain particles that they have collided with [Allredge and McGillivray, 1991]. Additionally, particles of lithogenic Si, too small to settle on their own have been seen to cosediment with phytoplankton aggregates in ocean waters [Brzezinski and Nelson, 1995; Kumar et al., 1998; Passow et al., 2001]. Transparent exopolymer particles (TEP) that are important for the coagulation of aggregates in the ocean [Allredge et al., 1993] have also been seen to scavenge inorganic particles from the water [Azetsu-Scott and Passow, 2004].

[31] Further support for the idea that it is the sinking of POC that is controlling the flux of ballast minerals comes from the saturation of the aggregates in these experiments with respect to ballast minerals at 2–3 weight-% organic C (Figure 4). In both the illite and calcium carbonate experiments, the fraction of the aggregates that was organic carbon decreased markedly once the initial suspended mineral concentration exceeded 100 or $400 \mu\text{g L}^{-1}$ (Figure 4), and then reached a plateau that could represent the "saturation" point of those aggregates for the mineral ballast. Notably, the plateau reached with calcium carbonate, the material whose flux is most strongly correlated with that of POC [François et al., 2002; Klaas and Archer, 2002], was $0.03 \mu\text{g C } \mu\text{g}^{-1}$ (Figure 4b). This value is very close to the 5 wt-% organic C observed by Armstrong et al. [2002] for sediment trap material. The plateau observed for illite in our experiments was slightly lower, at $0.02 \mu\text{g C } \mu\text{g}^{-1}$ (Figure 4a).

[32] Although it is tempting to deduce from the correlation between organic and inorganic fluxes into deep sea sediment traps that the inorganic fluxes are enhancing the organic ones [Armstrong et al., 2002; François et al., 2002; Klaas and Archer, 2002], the correlation on its own supports no such conclusion. The data reported here suggest that instead the POC to mineral ratio of material sinking through the deep sea is a function of the maximum amount of mineral material that organic aggregates are able to scavenge and incorporate as they sink [Passow, 2004]. If we are to understand the importance of suspended minerals for the transport of POC to the deep, and to discern whether

their role is to generally enhance or to generally diminish the fraction of primary production that reaches the seabed, we need to have a better quantitative understanding of the interactions between inorganic minerals and organic aggregates.

[33] **Acknowledgments.** We thank K. Schreiber for considerable help with the experiments, K.-U. Richter for technical assistance above and beyond the call of duty, Christian Hamm and H. Grobe for providing clays, A. Malzahn und S. Knotz for providing copepod fecal pellets, I. Zondervan for providing dried *T. weissflogii*, N. McCave and M. Rutgers van der Loeff for advice on particle concentrations, C. Klaas for insightful discussion, and two anonymous reviewers for excellent comments. This is AWI contribution awi-n15612.

References

- Allredge, A. L., and C. Gotschalk (1988), In situ settling behavior of marine snow, *Limnol. Oceanogr.*, **33**, 339–351.
- Allredge, A. L., and C. Gotschalk (1990), The relative contribution of marine snow of different origins to biological processes in coastal waters, *Cont. Shelf Res.*, **10**, 41–58.
- Allredge, A. L., and P. McGillivray (1991), The attachment probabilities of marine snow and their implications for particle coagulation in the ocean, *Deep Sea Res.*, **38**, 431–443.
- Allredge, A. L., and M. W. Silver (1988), Characteristics, dynamics, and significance of marine snow, *Prog. Oceanogr.*, **20**, 41–82.
- Allredge, A. L., U. Passow, and B. E. Logan (1993), The abundance and significance of a class of large, transparent organic particles in the ocean, *Deep Sea Res., Part I*, **40**, 1131–1140.
- Antia, A. N., et al. (2001), Basin-wide particulate carbon flux in the Atlantic Ocean: Regional export patterns and potential for atmospheric CO₂ sequestration, *Global Biogeochem. Cycles*, **15**, 845–862.
- Armstrong, R. A., C. Lee, J. I. Hedges, S. Honjo, and S. G. Wakeham (2002), A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POPC with ballast minerals, *Deep Sea Res., Part II*, **49**, 219–236.
- Avnimelech, Y., B. W. Troeger, and L. W. Reed (1982), Mutual flocculation of algae and clay: Evidence and implications, *Science*, **216**, 63–65.
- Azetsu-Scott, K., and U. Passow (2004), Ascending marine particles: Significance of transparent exopolymer particles (TEP) in the upper ocean, *Limnol. Oceanogr.*, **49**, 741–748.
- Barker, S., J. A. Higgins, and H. Elderfield (2003), The future of the carbon cycle: Review, calcification response, ballast and feedback on atmospheric CO₂, *Philos. Trans. R. Soc. London, Ser. A*, **361**, 1977–1998.
- Berelson, W. M. (2002), Particle settling rates increase with depth in the ocean, *Deep Sea Res., Part II*, **49**, 237–251.
- Billett, D. S. S., R. S. Lampitt, A. L. Rice, and R. F. C. Mantoura (1983), Seasonal sedimentation of phytoplankton to the deep-sea benthos, *Nature*, **302**, 520–522.
- Biscaye, P. E., and S. L. Eitrem (1977), Suspended particulate loads and transports in the nepheloid layer of the abyssal Atlantic Ocean, *Mar. Geol.*, **23**, 155–172.
- Brzezinski, M. A., and D. M. Nelson (1995), The annual silica cycle in the Sargasso Sea near Bermuda, *Deep Sea Res., Part I*, **42**, 1215–1237.
- Deuser, W. G., P. G. Brewer, T. D. Jickells, and R. F. Commeau (1983), Biological control of the removal of abiogenic particles from the surface ocean, *Science*, **219**, 388–391.
- Ferrari, G. M., F. G. Bo, and M. Babin (2003), Geo-chemical and optical characterizations of suspended matter in European coastal waters, *Estuarine Coastal Shelf Sci.*, **57**, 17–24.
- Field, C. B., M. J. Behrenfeld, J. T. Randerson, and P. Falkowski (1998), Primary production of the biosphere: Integrating terrestrial and oceanic components, *Science*, **281**, 237–240.
- François, R., S. Honjo, R. Krishfield, and S. Manganini (2002), Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochem. Cycles*, **16**(4), 1087, doi:10.1029/2001GB001722.
- Hamm, C. E. (2002), Interactive aggregation and sedimentation of diatoms and clay-sized lithogenic material, *Limnol. Oceanogr.*, **47**, 1790–1795.
- Hedges, J. I., and R. G. Keil (1995), Sedimentary organic matter preservation: An assessment and speculative synthesis, *Mar. Chem.*, **49**, 81–115.
- Heinze, C. (2004), Simulating oceanic CaCO₃ export production in the greenhouse, *Geophys. Res. Lett.*, **31**, L16308, doi:10.1029/2004GL020613.
- Ittekkot, V. (1993), The abiotically driven biological pump in the ocean and short-term fluctuations in atmospheric CO₂ contents, *Global Planet. Change*, **8**, 17–25.
- Jackson, G. A. (1994), Particle trajectories in a rotating cylinder: Implications for aggregation incubations, *Deep Sea Res., Part A*, **41**, 429–437.
- Klaas, C., and D. E. Archer (2002), Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochem. Cycles*, **16**(4), 1116, doi:10.1029/2001GB001765.
- Kumar, M. D., V. V. S. S. Sarma, N. Ramaiah, M. Gauns, and S. N. de Sousa (1998), Biogeochemical significance of transparent exopolymer particles in the Indian Ocean, *Geophys. Res. Lett.*, **25**, 81–84.
- McCave, I. N. (1975), Vertical flux of particles in the ocean, *Deep Sea Res.*, **22**, 491–502.
- Moulin, V., and C. Moulin (2001), Radionuclide speciation in the environment: A review, *Radiochim. Acta*, **89**, 773–778.
- Moulin, V., B. Amekraz, N. Barre, G. Planque, F. Mercier, P. Reiller, and C. Moulin (2004), The role of humic substances in trace element mobility in natural environments and applications to radionuclides, in *Humic Substances: Nature's Most Versatile Materials*, edited by E. Ghabbour and G. Davies, pp. 275–286, Taylor and Francis, Philadelphia, Pa.
- Passow, U. (2004), Switching perspectives: Do mineral fluxes determine particulate organic carbon fluxes or vice versa?, *Geochem. Geophys. Geosyst.*, **5**, Q04002, doi:10.1029/2003GC000670.
- Passow, U., R. F. Shipe, A. Murray, D. K. Pak, M. A. Brzezinski, and A. L. Allredge (2001), The origin of transparent exopolymer particles (TEP) and their role in the sedimentation of particulate matter, *Cont. Shelf Res.*, **21**, 327–346.
- Ragueneau, O., et al. (2000), A review of the Si cycle in the modern ocean: Recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy, *Global Planet. Change*, **26**, 317–365.
- Ridgwell, A. J. (2003), An end to the “rain ratio” reign?, *Geochem. Geophys. Geosyst.*, **4**(6), 1051, doi:10.1029/2003GC000512.
- Shanks, A. L., and E. W. Edmondson (1989), Laboratory-made artificial marine snow: A biological model of the real thing, *Mar. Biol.*, **101**, 463–470.
- Silver, M. W., and A. L. Allredge (1981), Bathypelagic marine snow: Deep-sea algae and detrital community, *J. Mar. Res.*, **39**, 501–530.
- Simpson, W. R. (1982), Particulate matter in the oceans—Sampling methods, concentration, size distribution, and particle dynamics, *Oceanogr. Mar. Biol. Annu. Rev.*, **20**, 119–172.
- Sundquist, E. T. (1993), The global carbon dioxide budget, *Science*, **259**, 934–941.

C. L. De La Rocha, Alfred-Wegener-Institut für Polar und Meeresforschung, Columbusstraße, D-27568 Bremerhaven, Germany. (crocha@awi-bremerhaven.de)

U. Passow, Alfred-Wegener-Institut für Polar und Meeresforschung, Am Handelshafen 12, D-27570 Bremerhaven, Germany. (upassow@awi-bremerhaven.de)