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Does a ballast effect occur in the surface ocean?

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[1] The oceanic biological carbon pump (BCP), a large (10 GT C yr^{-1}) component of the global carbon cycle, is dominated by the sinking (export) of particulate organic carbon (POC) from surface waters. In the deep ocean, strong correlations between downward fluxes of biominerals and POC (the so-called 'ballast effect') suggest a potential causal relationship, the nature of which remains uncertain. We show that similar correlations occur in the upper ocean with high rates of export only occurring when biominerals are also exported. Exported particles are generally biomineral rich relative to the upper ocean standing stock, due either to: (1) exported material being formed from the aggregation of a biomineral rich subset of upper ocean particles; or (2) the unfractionated aggregation of the upper ocean particulate pool with respiration then selectively removing POC relative to biominerals until particles are dense enough to sink. **Citation:** Sanders, R., P. J. Morris, A. J. Poulton, M. C. Stinchcombe, A. Charalampopoulou, M. I. Lucas, and S. J. Thomalla (2010), Does a ballast effect occur in the surface ocean?, *Geophys. Res. Lett.*, *37*, L08602, doi:10.1029/2010GL042574.

1. Introduction

[2] The oceanic biological carbon pump (BCP) is a major (10 GT C yr^{-1}) term in the global carbon cycle, mediated principally by the sinking of organic particles from the upper ocean [*Boyd and Trull*, 2007]. In order to sink, particles need to be both relatively large, to overcome viscous drag, and denser than seawater. Viscous drag is generally thought to be overcome via aggregation, however density poses a significant challenge given that particulate organic carbon has a density similar to that of seawater.

[3] In the deep ocean, strong correlations exist between fluxes of biominerals (opal and calcite) and particulate organic carbon (POC), suggestive of a potential causal link between the two – the so called 'ballast effect' [*Klaas and Archer*, 2002; *Armstrong et al.*, 2002]. Initially these relationships were interpreted to reflect the protection of some fraction of the sinking POC pool by association with biominerals, with the progression of the particle to the seafloor being facilitated by the density imparted by the heavy mineral fraction.

[4] However, interpretation moved on to consider the possibility that POC provides the 'glue' to stick together biomineral particles which would not sink without this factor [*Passow*, 2004]. Subsequent work has focused on elucidating the details of these mechanisms via a series of roller tank experiments, with the conclusions that scavenging of dissolved organic matter by biominerals and the scavenging of minerals by organic aggregates can both contribute to the formation of aggregates and help to explain the rather constant ratios of POC to biomineral found in deep ocean sediment traps [*Passow and De La Rocha*, 2006; *De La Rocha et al.*, 2008].

[5] In the upper ocean it is unknown whether similar relationships to those found in the deep ocean occur, and if they do, how we should interpret them. *Trull et al.* [2008] found limited evidence for a ballast effect in experiments conducted using an Indented Rotating Sphere (IRS) sediment trap during the VERTIGO voyages. It may therefore be that packaging by mesozooplankton is a more critical process in the upper ocean for imparting the excess density required for sinking. Conversely, *Lee et al.* [2009] found a significant effect of mineral ballast on sinking velocity in particles with an organic content of >40%. *Thomalla et al.* [2008] found that the surface ocean export flux of POC and biominerals were correlated based on an extremely limited (8 stations) suite of samples collected along an Atlantic Meridional Transect (AMT) cruise.

[6] Here, we present new data from a recent cruise in the subpolar North Atlantic (60°N, 20°W) that approximately doubles the database of simultaneous measurements of the downward fluxes of POC, opal and calcite previously presented by *Thomalla et al.* [2008]. We use these data to test whether a similar relationship to that found by *Klaas and Archer* [2002] exists in the surface ocean (<100 m), and to then examine whether the existence of such a relationship means anything for our understanding of the processes that underlie POC export.

2. Methods

[7] The export of POC and the biominerals, opal and calcite from the upper ocean were estimated using measured deficits of ^{234}Th in the mixed layer, coupled to particulate ^{234}Th:POC, calcite and opal ratios on particulate matter >53 μm at the base of the mixed layer. The standing stock of particulate matter >0.2 μm was evaluated using samples collected using a rosette sampler at multiple depths in the euphotic zone. Samples were obtained at 10 stations on R.R.S. *Discovery* cruise D321 in the Iceland Basin in August 2007. This dataset was combined with data collected on the 2004 AMT cruise (AMT14) using similar methods [*Poulton et al.*, 2006; *Thomalla et al.*, 2008]. On both cruises, standing stocks of all three phases were obtained via

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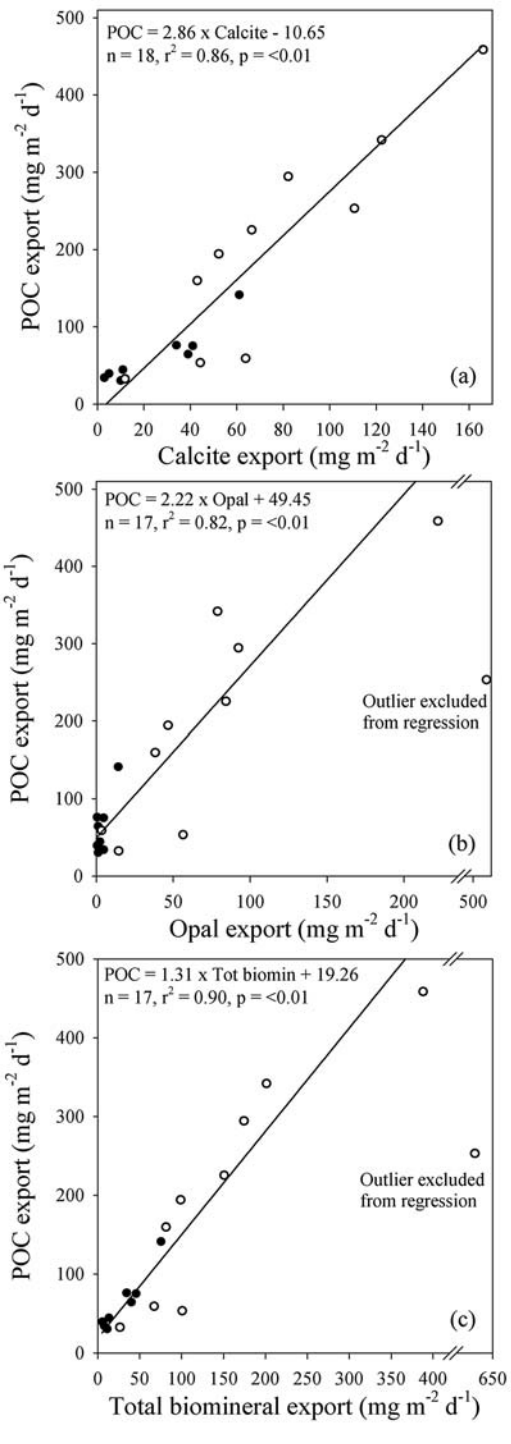

Figure 1. POC export as a function of (a) calcite, (b) opal and (c) total biomineral export at 18 sites in the subpolar, subtropical and tropical Atlantic Ocean. Full symbols are from the AMT study [*Thomalla et al.*, 2008]. Empty symbols are new observations reported here from the Iceland Basin in 2007 (auxiliary material). Regressions are model II regressions and exclude the highlighted outlier (auxiliary material). Regression analysis including the outlier gives: POC = 0.99 × Opal + 77.65, n = 18, $r^2 = 0.35$, $p < 0.01$ for Figure 1b; and POC = 0.79 × Tot biomin + 48.44, n = 18, $r^2 = 0.52$, $p < 0.01$ for Figure 1c.

the filtration of seawater samples and the subsequent analysis of the particles collected (see auxiliary material).[1]

[8] Water samples were taken from 10 depths within the upper water column using a rosette-CTD sampler. Total ^{234}Th was extracted from solution via precipitation with MnO_2 for 8 hours [*Rutgers van der Loeff et al.*, 2006]. The precipitate was filtered and the activity of ^{234}Th was measured using a low-level beta GM multicounter system (model Risø GM-25-5). Vertical profiles of ^{234}Th activity were converted to estimates of downward ^{234}Th flux using a one dimensional steady-state model. These fluxes were then converted to estimates of downward particle flux using the ^{234}Th:POC or ^{234}Th:biomineral ratio on large (>53 μm) particles collected as described below. Several authors have noted that the thorium partition coefficient is often larger for calcite and POC than for opal [e.g., *Chase et al.*, 2002], which implies a potential overestimation of opal flux. However, since the mass fluxes of POC are approximately twice as large as those of either biomineral (Figure 1), the dominant control over particle/thorium ratios is likely to have been the organic carbon content of the sampled aggregates.

[9] Large particulate matter was collected using an *in situ* Stand Alone Pumping System (SAPS) deployed for 1.5 hrs just beneath the mixed layer. Approximately 1500–2000 L of seawater was filtered through a 53 μm Nitex screen. Particles were rinsed off the screen using thorium-free seawater, and the particle suspension quantitatively split into four subsamples using a Folsom splitter. Each split was then analyzed for one of the following: ^{234}Th, POC, calcite and opal.

[10] Biogenic silica (opal) samples were filtered onto 0.2 μm membrane filters, digested with sodium hydroxide (0.2 M, 80°C, 4 hours) and neutralized with 0.1 M hydrochloric acid [*Brown et al.*, 2003]. Silicate concentrations in the resultant digest were measured on D321 using a Skalar San Plus autoanalyser [*Sanders and Jickells*, 2000] or on AMT on a Bran and Luebbe autoanalyser. Calcite samples were filtered onto 0.2 μm polycarbonate filters, rinsed with ammonium solution, and calcium concentrations determined using Inductively Coupled Plasma Optical Emission Spectroscopy [*Thomalla et al.*, 2008]. POC samples were filtered onto pre-combusted GFF filters, fumed and analysed using a Thermo Finnegan Flash EA1112 Elemental Analyser [*Thomalla et al.*, 2008].

3. Results and Discussion

[11] Figure 1 shows the relationships between biomineral (opal and calcite) and POC export following *Klaas and Archer* [2002]. We found strong, statistically robust relationships between POC and biomineral export from the euphotic zone in a diverse array of ecosystems including subpolar, subtropical and tropical environments. This builds on the relationship established in our earlier work [*Thomalla et al.*, 2008] extending it into a wider range of opal, calcite and POC flux rates. It is, in our view, an extremely significant result as it implies that the conceptual framework established by *Klaas and Archer* [2002] regarding the potential role of ballasting biominerals in mediating down-

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2010GL042574.

ward POC flux in the deep ocean, can be extended into the upper ocean. The slopes of the relationships are significantly steeper than those reported by *Klaas and Archer* [2002], consistent with the known loss of POC as material sinks, relative to the lower fraction of exported biomineral which is lost [*Poulton et al.*, 2006; *Thomalla et al.*, 2008]. The slopes for calcite (2.86) and opal (2.22), which are dominated by observations from the North Atlantic suggest that both phases play a significant role in driving downward carbon flux in the region in late summer following intense diatom and coccolithophore blooms in the region. The regression coefficient for opal is slightly lower than that for calcite, and is further reduced if the outlier excluded from the regression is included (Figure 1). This, coupled to the steeper gradient for calcite, implies a more significant role for calcite in any ballasting process, as suggested by *Klaas and Archer* [2002].

[12] If the existence of such a relationship is diagnostic of a ballast effect, then we can say that one does occur in surface waters. However, such a relationship could simply result from there being a relatively constant biomineral to POC ratio in sinking matter, with the inclusion of biomineral within the exported pool being purely incidental and unrequired for particle export to occur. Under these circumstances the term ‘ballast effect’ is of limited value. We consider that for the term ‘ballast effect’ to mean anything, it must be the case that either: (1) it is an explicit requirement for export to occur that biominerals are exported in parallel or (2) that exported particles are richer in biomineral (and therefore probably denser) than suspended particles.

[13] The first possibility can be excluded by inspection of Figure 1. It is clear that detectable POC export can occur accompanied by negligible (although not unmeasurable) biomineral export; implying that biominerals are not an explicit requirement for POC export to occur. These ‘near zero’ offsets on the y-axis imply that the highest rates of POC export were associated with the most biomineral rich exported material. The second possibility can be evaluated by considering whether the exported material is stoichiometrically similar to the suspended particulate pool in the upper ocean; if it is persistently biomineral rich relative to the upper ocean pool then it would signify that the inclusion of biominerals probably facilitates sinking. Initially, we consider each biomineral individually to determine whether either is persistently richer in the sinking material relative to the suspended material. Figure 2 shows POC/biomineral (opal and calcite) ratios in the exported particles sampled using the SAPS and in the standing stock of particulate material in the water column. At 72% (13 from 18) of the stations sampled the standing stock POC/opal or POC/calcite ratio was larger or equal to the corresponding ratio in the exported material (Figures 2a and 2b).

[14] Exceptions to this rule for calcite were mainly derived from the Iceland Basin (Figure 2a) and for opal from the AMT study (Figure 2b), thus at some stations the exported material was relatively calcite or opal poor compared to the ambient upper ocean pool. This may have been due to a compensating effect from the other biomineral - in Figure 2c at 15 out of 18 stations the POC/biomineral ratio in exported particles is lower than in the upper ocean. This suggests that most exported particles have a higher density than the upper ocean standing stock, a factor which may lead to their export.

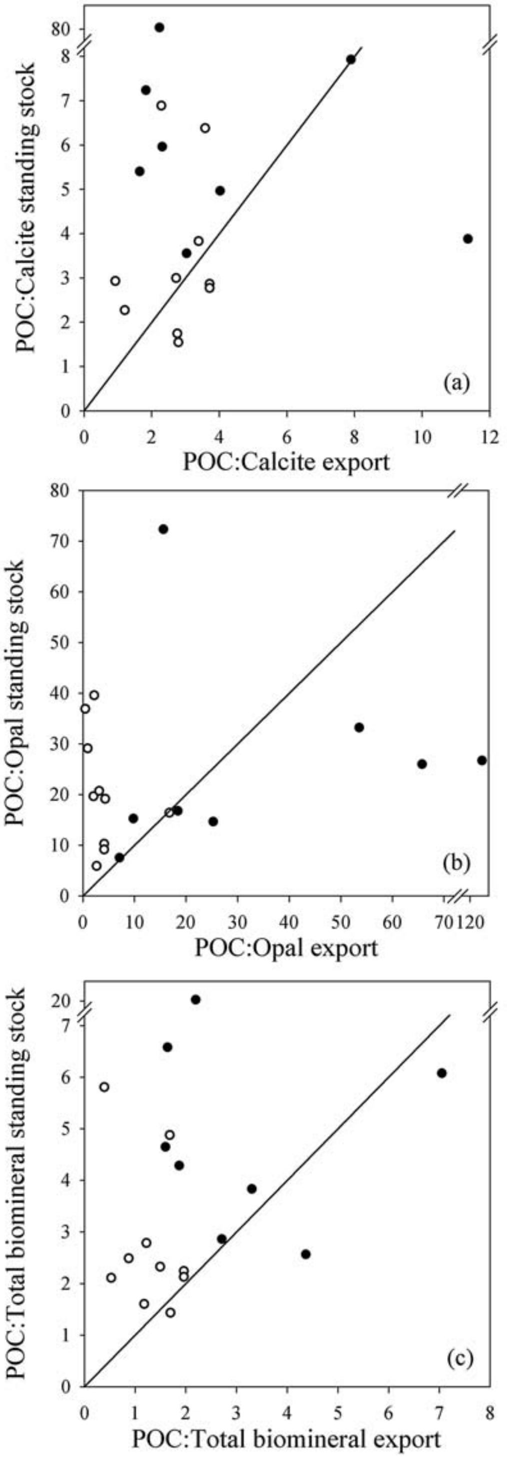

Figure 2. POC (a) calcite, (b) opal and (c) total biomineral ratios in exported and upper ocean particulate pools at 18 sites in the subpolar, subtropical and tropical Atlantic Ocean. Full symbols are from the AMT study [*Thomalla et al.*, 2008]. Empty symbols are new observations reported here from the Iceland Basin in 2007 (auxiliary material). Note the broken axis required to include all data points.

[15] We consider two explanations for this: either the upper ocean pool coagulates in a fractionated manner with the biomineral rich fraction then sinking; or, alternatively, minimal fractionation occurs during aggregate formation, with respiration selectively removing POC from these aggregates until they become dense enough to sink. We hypothesize that the known greater lability of POC compared to biominerals (which manifests itself as a larger remineralisation length scale for biominerals compared to organic carbon [*Thomalla et al.*, 2008]) causes POC but not biominerals to be respired within the euphotic zone until the particle acquires sufficient excess density to sink.

[16] If this is the case then there is no reason why the POC/biomineral composition of the suspended particulate pool should be related to the POC/biomineral ratio of the exported pool, as long as its higher – hence only weak correlations are found between the fractional concentration of biomineral in the standing stock and the magnitude of POC export. This hypothesized mechanism provides an explanation for the lag frequently observed between production and export in bloom situations – blooms only begin to export organic carbon once sufficient POC has been respired for the aggregates to exceed the critical excess density required to sink. There was no statistically robust relationship between the relative biomineral richness of exported particles and the rate of POC export, although two of the three stations where POC/biomineral ratios in the exported material were <1 also had high POC export rates, suggesting a potentially causative relationship.

[17] Distinguishing between the two hypotheses presented above (selective aggregation vs minimal fractionation followed by preferential respiration of organic carbon relative to biomineral dissolution) would ideally be accomplished by using the same sampling technique to sample both the small (suspended) and large (sinking) size fractions. However, this is almost impossible as Niskin bottles sample so few sinking particles. A further critical issue that may invalidate our conclusion that the exported field is biomineral rich relative to the ambient pool, is that of selective sampling by the SAPS, which we used to harvest large, nominally sinking particles. However, separating the sinking from the suspended pool of material is a non trivial problem and the arguments made above depend critically on our ability to do so. Historically, surface tethered sediment traps were the method of choice to collect upper ocean particle export. However, these have been shown to be unreliable due to swimmer contamination and turbulence effects at the trap mouth [*Buesseler et al.*, 2007]. Thus examining the issue of selective sampling by SAPS is non trivial, as it is unclear whether sediment trap derived fluxes are absolutely correct.

[18] To address this issue, two groups have constructed neutrally buoyant sediment traps that significantly reduce the problems of surface tethered sediment traps [*Buesseler et al.*, 2000; *Lampitt et al.*, 2008] and which can therefore be used to test the selective sampling of SAPS. We deployed neutrally buoyant sediment traps (PELAGRA) in the southern Indian Ocean during the CROZEX study [*Salter et al.*, 2007] in parallel with SAPS and Niskin bottle sampling of the particulate field. The POC/opal ratios of sediment trap derived, SAPS harvested and Niskin bottle collected particles were 2.7 ± 0.9, 1.2 ± 0.1 and 4.7 ± 0.5 respectively (mean ± se, n = 7). The ratios in SAPS and PELAGRA collected particles are not absolutely the same, which is likely caused by the immense difficulties of undertaking such a comparison perfectly, with issues such as variable sampling depths and durations and the unknown precise location of the PELAGRA traps relative to the vessel being key in this regard. However, it is clear that both sediment trap collected and SAPS harvested particles were relatively carbon poor compared to the ambient pool, validating the conclusions derived here and suggesting that the ballast effect may also operate in the Southern Ocean. This conclusion must be viewed as tentative in the light of the organic carbon content of PELAGRA collected particles being higher than SAPS collected samples.

[19] The mechanisms by which the particles we sampled formed into their relatively biomineral rich state remains unresolved from the data presented here. Transparent Exopolymer Particles (TEP) mediated aggregation, the gluing together of biomineral particles by sticky organic carbon [*Passow*, 2004], the adsorption of organic particles by biominerals [*Klaas and Archer*, 2002], the compression of material during zooplankton feeding, or the respiration of POC within aggregates could all provide the mechanisms by which particles become large enough and dense enough to sink. An additionally unconstrained term that might be important is lithogenic material, about which we have unfortunately no information.

[20] It is quite clear however that: (a) there is a strong relationship between POC and biomineral export; (b) that elevated rates of POC export only occur when biominerals are also exported; and (c) that the exported material is generally biomineral rich (dense) relative to the upper ocean pool, with the ratio of biomineral/POC in exported material being largest when POC export fluxes are largest (Figure 1c). For these reasons we believe that a ballast effect does occur in the upper ocean. It is noteworthy that the colonial prymnesiophyte *Phaeocystis* sp. is only weakly involved in export whereas the two main groups of phytoplankton involved in producing biominerals, diatoms and coccolithophores, generate significant sedimentation signals, supporting the suggestion that a ballast effect may occur.

[21] Since biominerals are clearly required for elevated rates of POC export to occur (Figure 1), and it is the export of POC that we are primarily (although not exclusively) interested in, an important question is the concentration (and possibly production) of which phase is rate limiting for the process of POC export. Most POC produced in the upper ocean is currently respired and not exported [*Poulton et al.*, 2006; *Thomalla et al.*, 2008], thus more POC might therefore be exported in an alternative system where more biominerals are being produced. To first order, opal production is controlled by silicic acid concentration with its degradation being promoted by enhanced temperature [*Brown et al.*, 2003; *Cermeno et al.*, 2008]. Deepening of the wind mixed layer and an increase in surface temperature, as predicted under climate change scenarios [*Sarmiento et al.*, 2004] are likely to reduce both the production of opal and increase its dissolution rate. Ocean acidification [*Caldeira and Wickett*, 2003] will lead to a chemical environment favourable to calcite dissolution, whereas the controls on calcite production also include a favourable nutrient environment [*Zondervan*, 2007]. Thus predicted changes in ocean pH are likely to reduce any ballast mediated flux of organic matter from the upper ocean.

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