

Letter Section

Colloid aggregation in seawater

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ABSTRACT

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Aggregation of small colloids ($< 0.2 \mu\text{m}$) is common in ocean waters and leads to agglomerates that are several microns in size. These aggregates are the most abundant macroparticles ($> 1.0 \mu\text{m}$) in mid-depth and deep waters of the Atlantic and Pacific Oceans, with concentrations in the order of 10^9 colloid aggregates ml^{-1} . The fractal structures of these aggregates are characteristic of both reaction-limited and diffusion-limited processes, indicating that colloidal dynamics vary widely in seawater. Aggregation can greatly enhance the involvement of marine colloidal matter in biological and sedimentation processes.

Small colloids (5–200 nm) have recently been found to be the most abundant particles occurring in seawater, with concentrations reaching 10^9 particles per ml (Wells and Goldberg, 1991, 1992, 1993). They are mainly organic though they also may contain some metals (Wells and Goldberg, 1991). It now becomes essential to distinguish whether substances in sub-micron filtered seawater occur in colloidal or soluble phases because each will have unique behaviors. Theoretical arguments combined with limited data from laboratory experiments suggest that the aggregation of marine colloidal matter is an important mechanism for transferring dissolved substances into the macroparticle ($> 1.0 \mu\text{m}$) size range (Farley and Morel, 1986; Honeyman and Santschi, 1989, 1991). Such a process would alter our understanding of the fundamental constraints to the biogeochemical cycling of carbon and metals, but so far there has been little

evidence that colloid aggregation is significant in the oceans.

We report that small colloids are extremely abundant in the open ocean and agglomerations of these colloids constitute a major component of the macroparticulate fraction in coastal and oceanic waters of the North Atlantic and North-west Pacific. Small colloid concentrations were near 10^9 particles per ml at three open ocean sites (the Sargasso Sea and equatorial Pacific—Wells and Goldberg, 1993), similar to those concentrations in shelf waters off California (Wells and Goldberg, 1991, 1992) and Nova Scotia (Wells and Goldberg, 1993). The size spectra of small colloids in the open ocean show increases in colloid numbers with decreasing size, often nearly logarithmic in surface waters (Fig. 1(A)). Colloids ≤ 60 nm appeared in transmission electron microscope images as spherical clusters of heterogeneous 2–5 nm sized granules, some of which were darker than others (Fig. 1(B)); larger colloids (60–200 nm) typically were due to coalescence of these clusters. The size spectra and morphology of small colloids were indistin-

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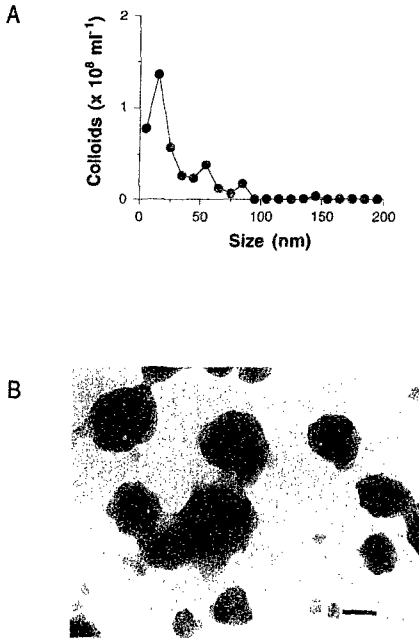


Fig. 1. (A) Size distribution of small colloids at 20-m depth in the northwest Pacific ($25^{\circ} 00' N$ $165.00^{\circ} 00' E$). The colloids were collected by ultracentrifugation (Beckman L7 (Beckman Instruments, USA)) in a swing-bucket rotor (SW41 (Beckman Instruments, USA)) at $288,000 g$ for 4.1 h at $25^{\circ}C$. Colloids were sedimented directly onto 200-mesh Cu transmission electron microscope (TEM) specimen grids (coated with carbon-stabilized formvar — Ted Pella[®], Reading, CA, USA) supported in specially constructed holders in the bottom of 13-ml polyallomer centrifuge tubes. Details of the method are described elsewhere (Wells and Goldberg, 1992). Samples were poisoned ($3 \mu M HgCl_2$) and stored cold ($5^{\circ}C$) until ultracentrifugation ashore. Independent tests showed that the addition of $HgCl_2$ preserves the abundance, morphology and size distribution of small colloids. After rinsing, the specimen grids were examined in a Phillips (USA) CM30 transmission electron microscope operated at 100 kv and the size distributions measured by image analysis of digitized images. The increase in colloids numbers with decreasing size is likely to be considerably more pronounced than indicated here because very small colloids (5–30 nm) are not sedimented quantitatively with only 4 h of ultracentrifugation. (B) TEM micrograph of small colloids from 2000 m depth in the Sargasso Sea ($36^{\circ} N$ $63^{\circ} 30' W$). Small granules 2–5 nm appear to make up these colloids which are nearly identical in appearance to those found in near-shore environments (Wells and Goldberg, 1991, 1992). Scale bar is 25 nm.

guishable from those in near-shore waters (Wells and Goldberg, 1991, 1992) which are mainly organic in nature and have been found to form in cultures of phytoplankton and bacteria (Wells and Goldberg, 1991). Thus, the biologically derived, small colloid phase is distributed abundantly in both near-shore and offshore environments.

Our results support the view that two pools of organic carbon occur in sub-micron filtered ocean waters: truly dissolved and colloidal organic carbon (Koike et al., 1990). Though sub-micron filtered organic carbon typically is classed as 'dissolved organic carbon' (DOC) in the literature, this term is non-rigorous and we do not use it here. We calculate that in the Sargasso Sea small colloids account for 1–45% of the sub-micron filterable organic carbon concentrations measured by high-temperature catalytic oxidation (Kepkay and Wells, 1992) (based on the estimated total colloid volume and an assumed density of $1.4 g cc^{-1}$ for vacuum-dried organic matter 50% C by weight). (This assumed colloid density is higher than the $1.1 g cc^{-1}$ used in Wells and Goldberg, 1991 as we now believe that drying increases colloid density through closer packing of the organic matrix.) The largest colloidal component occurred in surface waters, particularly near the seasonal thermocline. These findings have particular significance with respect to current perceptions of the marine carbon cycle, as will be discussed shortly.

The commonalities in small colloid morphology, abundance and size distributions in shelf and open ocean waters suggest that a general mechanism of colloid formation and removal occurs among these diverse oceanic regimes. Clearly, these colloids have a biogenic origin but what is the fate of this colloid fraction? Because colloids do not sink, their removal from seawater will depend upon either their dissolution (through thermochemical, biological or photochemical processes) or their aggregation to form larger particles (though capture by suspension feeders also maybe important in some cases (Flood et al., 1992)). However, a dissolution-

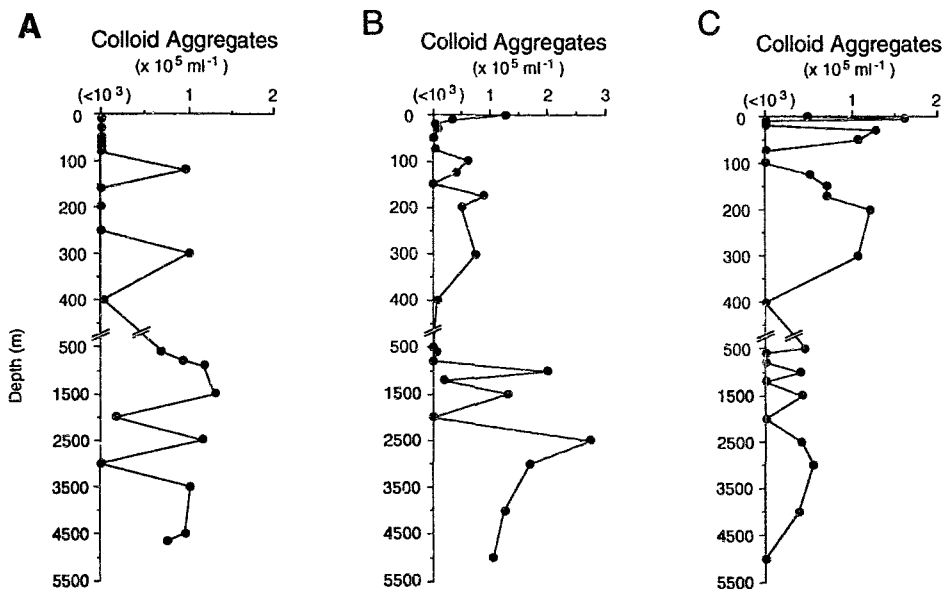


Fig. 2. Profiles of the concentrations of colloid aggregates > 500 nm in size at the three oceanic stations: (A) the Sargasso Sea ($36^{\circ} 30' \text{ W}$), (B) the northwest Pacific ($45^{\circ} 00' \text{ N } 165.00^{\circ} 00' \text{ E}$), and (C) the sub-tropical Pacific ($25^{\circ} 00' \text{ N } 165.00^{\circ} 00' \text{ E}$). Stations (A) and (C) were in oligotrophic regions while (B) was situated in a highly productive region of the Kuroshio current, the Pacific analog to the North Atlantic Gulf Stream. More than 90% of these aggregates were $1\text{--}5 \mu\text{m}$ in size. Aggregate concentrations were calculated from counts of aggregates in low magnification TEM micrographs.

dominated colloid system is unlikely because dissolution would result in fewer particle numbers with decreasing size (owing to higher surface area:volume ratios), which is exactly opposite to the trends found. The colloid size spectra instead are consistent with those in aggregation-dominated marine macroparticle suspensions (McCave, 1986), pointing to coalescence with other colloids as the principal mechanism removing small colloids.

Large ($> 1.0 \mu\text{m}$) cluster-cluster aggregates of small colloids occur in shelf waters and at all three open ocean sites. Aggregate concentrations in the open ocean were on the order of 10^5 aggregates per ml (Figs. 2(A), (B), (C)) and similar concentrations occurred in near-shore waters. Colloid aggregates dominated the macroparticle size range in deep waters (> 500 m) of the North

Atlantic and northwest Pacific. They accounted for $89 \pm 9.1\%$ of $1\text{--}5 \mu\text{m}$ sized macroparticles at the Sargasso station (11 samples from 500–5000 m) while in the northwest Pacific values were $97 \pm 8.2\%$ (eight depths from 500–5000 m) and $96 \pm 4.7\%$ (six depths from 500–5000 m) at 45° N and 25° N , respectively. These aggregates were not artifacts created during ultracentrifugation; suspensions of colloidal latex (89 nm, Seradyn, Indianapolis, IN, USA) and silica (22 nm, Ludox[®], Dupont, Wilmington, DE, USA) show insignificant aggregation when added to seawater at similar concentrations and ultracentrifuged. (Both natural and synthetic surfaces rapidly acquire organic coatings when added to seawater (Neihof and Loeb, 1972; Newton and Liss, 1989) and thus synthetic colloids would exhibit the surface characteristics of natural

particles.) Further, the number of colloid aggregates in the samples was not related to the concentration of small colloids.

Colloid aggregates occurred principally within and below the main thermocline (500–1000 m) at the Sargasso station (Fig. 2(A)) while in the Pacific, colloid aggregates were distributed erratically throughout the water column, including near-surface waters (Figs. 2(B), (C)). The two Pacific profiles display remarkably similar features in spite of being separated by 1200 km, suggesting the presence of extensive aggregate 'horizons' in both surface and deep-ocean waters. Even so, aggregate concentrations were higher in deep waters underlying the highly productive Kuroshio current (Fig. 2(B)) than at the two oligotrophic sites (Figs. 2(A), (C)), indicating that the intensity of colloidal processes can differ within these 'horizons'. Clearly, the non-homogeneous distribution of colloid aggregates with depth indicates that they are quite reactive, with residence times considerably less than oceanic mixing times of millennia. The systematics of colloid aggregate distribution needs to be explored.

Two broad aggregate morphologies were found that are characteristic of the two limiting regimes of colloid aggregation (Figs. 3(A), (B)). These regimes are general for all colloid suspensions, regardless of composition, and are described by fractal mechanisms. Diffusion-limited colloid aggregation (DLCA) comes about when the rate of aggregate formation is limited solely by colloid encounter rates (Lin et al., 1989, 1990b) a very rapid process that forms open, tenuous structures (Fig. 3(A)). By contrast reaction-limited colloid aggregation (RLCA) occurs when a significant repulsive force between colloids must be overcome by thermal activation in order for adhesion to occur (Lin et al., 1989, 1990a) RLCA aggregates form slowly and have more condensed structures (Fig. 3(B)). Most marine colloid aggregates were of the RLCA-type, though DLCA-type aggregates were sometimes observed in near-surface waters. The presence of both DLCA and RLCA type colloid

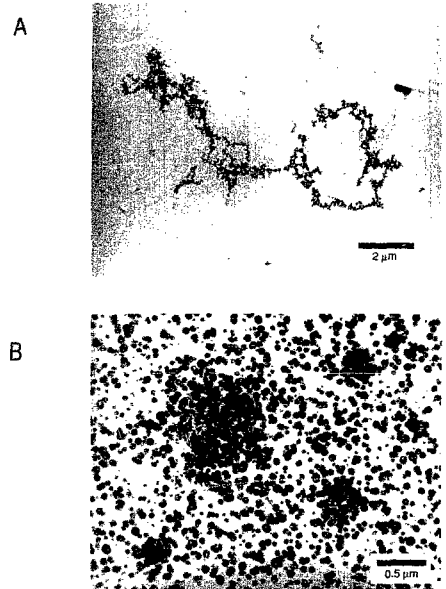


Fig. 3. Cluster-cluster aggregations of small colloids collected from near-shore and offshore environments. Scale bars are: (A) 2 μm , (B) and (C) 0.5 μm and (D) 0.1 μm . (A) From 80-m depth in Santa Monica basin, California, in September 1990. (B) From 125-m depth in San Clemente basin, California, in February 1991. (C) From 2500-m depth in the western Sargasso Sea (36° 00' N 63° 30' W) in April 1991. (D) Enlarged view of the aggregate in (C) showing a mucus-like material interbridging the component colloids. The aggregate in (A) displays an open, tenuous structure that is characteristic of DLCA while more compact colloid aggregates as in (B) and (C) are typical of RLCA regimes. The aggregates exhibit fractal dimensions of 1.3 (A) and ~ 1.5 (B, C) as determined by Richardson plot of the structured walk technique (Kaye et al., 1987). These fractal dimensions are smaller than calculated for DLCA and RLCA aggregation by other methods (Lin et al., 1990a, 1990b), though the differences between types are similar in magnitude (Lin et al., 1989).

aggregates indicates that colloid dynamics vary greatly in seawater. Close examination of many deep-water aggregates shows that the component colloids are interbridged by mucus-like materials (Fig. 3(D)), indicating that biopolymers are involved in their formation.

Several implications arise from colloid aggregation in seawater: in addition to involving col-

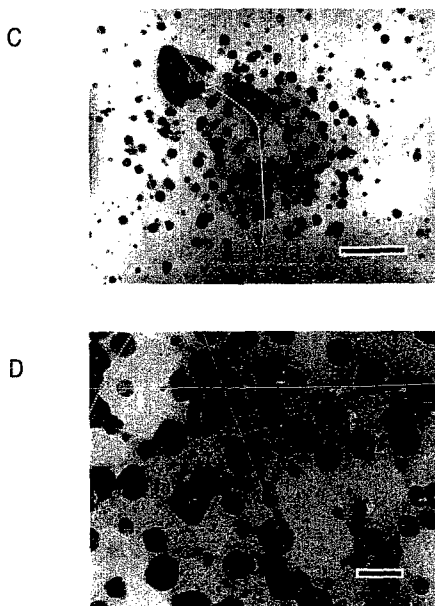


Fig. 3. Continued.

loidal organic matter in sedimentary processes, aggregation will physically regenerate this carbon by packaging it into larger units more accessible for biological utilization (Shimeta and Jumars, 1991; Kepkay and Johnson, 1988, 1992; Kepkay et al., 1990). Because the release of surface-active biopolymers could greatly facilitate aggregation rates by modifying surface charge or by colloid interbridging, the simple disappearance of non-filterable, sub-micron organic carbon during microbial incubations in seawater is not sufficient evidence to demonstrate its direct utilization by bacteria. The 'microbial loop', therefore, maybe less important as a direct sink for non-filterable organic carbon than generally is believed. Crucially important to our understanding of carbon cycling in seawater will be determining the degree of coupling between the soluble, colloidal and particulate organic carbon reservoirs. Moreover, both dissolved and colloidal metals also may become

incorporated into this aggregation stream, which would greatly facilitate their removal from seawater. Our findings of high abundances of small colloids and of their agglomerations provide only 'snap-shots' of what presumably is a highly dynamic process. Clearly, the next critical step will be to determine the time-scales of formation and destruction of these agglomerates in surface and deep-ocean waters.

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REFERENCES

- Farley, K.J. and Morel, F.M.M., 1986. Role of coagulation in the kinetics of sedimentation. *Environ. Sci. Technol.*, 20: 187-196
- Flood, P.R., Deibel, D. and Morris, C.C., 1992. Filtration of colloidal melanin from seawater by planktonic tunicates. *Nature*, 355: 630-632.
- Honeyman, B.D. and Santschi, P.H., 1989. A Brownian pumping model for oceanic trace metal scavenging: evidence from Th isotopes. *Deep-Sea Res.*, 47: 951-992.
- Honeyman, B.D. and Santschi, P.H., 1991. Coupling adsorption and particle aggregation: laboratory studies of 'colloidal pumping' using ^{59}Fe labeled hematite. *Environ. Sci. Technol.*, 25: 1739-1747.
- Kaye, B.H., Clark, G.G., Leblane, J.E. and Trottier, R.A., 1987. Image analysis procedures for characterizing the fractal dimension of fineparticles. *Part. Charact.*, 4: 63-66.
- Kepkay, P.E. and Johnson, B.D., 1988. Microbial response to organic particle generation by surface coagulation in seawater. *Mar. Ecol. Prog. Ser.*, 48: 193-198.
- Kepkay, P.E. and Johnson, B.D., 1992. Colloid transport and bacterial utilization of oceanic DOC. *Deep-Sea Res.*, 39: 855-869.
- Kepkay, P.E. and Weils, M.L., 1992. Dissolved organic carbon in North Atlantic surface waters. *Mar. Ecol. Prog. Ser.*, 80: 275-283.
- Kepkay, P.E., Harrison, W.G. and Irwin, B., 1990. Surface coagulation, microbial respiration and primary production in the Sargasso Sea. *Deep-Sea Res.*, 37: 145-155.
- Koike, I., Hara, S., Terauchi, K. and Kogure, K., 1990. Role

- of sub-micron particles in the oceans. *Nature*, 345: 242-244.
- Lin, M.Y., Lindsay, H.M., Weitz, D.A., Ball, R.C., Klein, R. and Meakin, P., 1989. Universality in colloid aggregation. *Nature*, 339: 360-362.
- Lin, M.Y., Lindsay, H.M., Weitz, D.A., Ball, R.C., Klein, R. and Meakin, P., 1990a. Universal reaction-limited colloid aggregation. *Phys. Rev. A*, 41: 2005-2020.
- Lin, M.Y., Lindsay, H.M., Weitz, D.A., Klein, R., Ball, R.C. and Meakin, P., 1990b. Universal diffusion-limited colloid aggregation. *J. Phys. Condens. Matter*, 2: 3090-3113.
- McCave, I.N., 1986. Size spectra and aggregation of suspended particulates. *Deep-Sea Res.*, 31: 329-352.
- Neihof, R.A. and Loeb, G.I., 1972. The surface charge of particulate matter in seawater. *Limnol. Oceanogr.*, 17: 7-16.
- Newton, P.P. and Liss, P.S., 1989. Surface charge characteristics of oceanic suspended particles. *Deep-Sea Res.*, 36: 759-767.
- Shimeta, J. and Jumars, P.A., 1991. Physical mechanisms and rates of particle capture by suspension-feeders. *Oceanogr. Mar. Biol. Annu. Rev.*, 29: 191-257.
- Wells, M.L. and Goldberg, E.D., 1991. Occurrence of small colloids in sea water. *Nature*, 353: 342-344.
- Wells, M.L. and Goldberg, E.D., 1992. Marine sub-micron particles. *Mar. Chem.*, 40: 5-18.
- Wells, M.L. and Goldberg, E.D., 1992. The distribution of colloids in the North Atlantic and Southern Oceans. *Limnol. Oceanogr.*, (in review).