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## Phosphorus distribution in sinking oceanic particulate matter

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## Abstract

Despite the recognition of the importance of phosphorus (P) in regulating marine productivity in some modern oceanic systems and over long timescales, the nature of particulate P within the ocean is not well understood. We analyzed P concentration in particulate matter from sediment traps and selected core tops from a wide range of oceanic regimes: open ocean environments (Equatorial Pacific, North Central Pacific), polar environments (Ross Sea, Palmer Deep), and coastal environments (Northern California Coast, Monterey Bay, Point Conception). These sites represent a range of productivity levels, temporal (seasonal to annual) distributions, and trap depths (200-4400 m). P associations were identified using an operationally defined sequential extraction procedure. We found that P in the sediment traps is typically composed of reactive P components including acid-insoluble organic P (~40%), authigenic P (~25%), and oxide associated and/or labile P (~21%), with lesser proportions of non-reactive detrital P depending on location (~13%). The concentrations and fluxes of all particulate P components except detrital P decrease or remain constant with depth between the shallowest and the deepest sediment traps, indicating some regeneration of reactive P components. Transformation from more labile forms of P to authigenic P is evident between the deepest traps and core top sediments. Although for most sites the magnitudes of reactive P fluxes are seasonally variable and productivity dependent, the fractional associations of reactive P are independent of season. We conclude that P is transported from the upper water column to the sediments in various forms previously considered unimportant. Thus, acid-insoluble organic P measurements (typically reported as particulate organic P) likely underestimate biologically related particulate P, because they do not include the labile, oxide-associated, or authigenic P fractions that often are or recently were biologically related. Organic C to reactive P ratios are typically higher than Redfield Ratio and are relatively constant with depth below ~300 m suggesting that preferential regeneration of P relative to C occurs predominantly at shallow depths in the water column, but not deeper in the water column (>300 m). The view of P cycling in the oceans should be revised (1) to include P fractions other than acid-soluble organic P as important carriers of reactive P in rapidly sinking particles, (2) to include the efficient transformation of labile forms of P

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to authigenic P in the water column as well as in sediments, and (3) to consider the occurrence of preferential P regeneration at very shallow depths.

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## 1. Introduction

Despite the recognition of the importance of P in regulating marine productivity in some modern oceanic systems (e.g., Karl et al., 1995; Wu et al., 2000) and over long timescales (e.g., Tyrrell, 1999), P cycling within the ocean is not well understood (e.g., Delaney, 1998; Benitez-Nelson, 2000). The major carrier phase of P to marine sediments is thought to be particulate organic matter, although few direct measurements of particulate P flux in the oceans have been made and even fewer measurements have determined the organic P fraction (Benitez-Nelson, 2000). Little is known about the distribution of P within different fractions in marine particulate matter, about the temporal or spatial variability in this distribution, or about the differences in P distribution in marine particulate matter compared to marine sediments.

Mass balance studies of the P cycle indicate that the primary input of P to the oceans is the dissolved P flux from rivers (Froelich et al., 1982; Delaney, 1998, and references therein). This P is utilized by organisms and transformed into the particulate fraction. Particulate P is recycled in the water column as manifested by the "nutrient type" distribution of dissolved P in the water column; however, the processes of recycling are poorly understood (Benitez-Nelson, 2000). A few recent studies have pioneered the exploration of the nature of particulate P in the water column (e.g., Clark et al., 1998, 1999; Loh and Bauer, 2000; Paytan et al., 2003; Benitez-Nelson et al., 2004), but much remains to be determined regarding the distribution, composition, and spatial and temporal variability of particulate P. A small fraction (~1%) of the reactive particulate P escapes regeneration in the water column and is buried in the sediments (e.g., see discussion in Delaney, 1998). In open ocean sites, it is thought that much of the P is delivered to the sediment–water interface primarily in association with organic material and secondarily with oxyhydroxides (e.g., Delaney, 1998). Through the process of sink switching, these phases are transformed to authigenic P in the sediments with increasing age and depth (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1995, 1996; Slomp et al., 1996; Delaney and Anderson, 1997, 2000; Anderson et al., 2001; Faul et al., 2003). A fraction of this P may also diffuse out of the sediments (e.g., McManus et al., 1997).

In sediments, sink switching occurs when P is liberated into porewaters as a result of microbial remineralization of organic matter and/or microbial iron reduction of organic P and/or oxide-associated P. Authigenic carbonate fluorapatite (CFA) is formed as a result (Ruttenberg and Berner, 1993). When the ion activity product is equal to or exceeds the solubility product for authigenic CFA, precipitation of this mineral within the sediment is favored (Ruttenberg and Berner, 1993). Ruttenberg and Berner (1993) suggested that when the decrease in organic P in sediments mirrors the increase in authigenic P in sediments, with little change in total P, formation of CFA is implied. Therefore, they argue, this authigenic P constitutes a component of the oceanic reactive P sink (Ruttenberg and Berner, 1993). Reactive P in this context refers to any P that is or has been associated at some point with living (or dead) organisms and thus consists of labile P, organic P, P adsorbed onto or associated with oxide particles, and authigenic P (CFA), and does not necessarily imply bioavailability.

To address questions about the nature of oceanic sinking particulate P, we present the concentrations and association of different, operationally defined, components of particulate P in various sediment trap and core top sediment samples. Our objectives are to characterize the nature of particulate P, its transformations through the water column, and any spatial or temporal trends in distribution. This is important for Download English Version:

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