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Distribution, source and chemical speciation of phosphorus in surface sediments of the central Pacific Ocean

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ABSTRACT

The abundance of five forms of phosphorus (P) in surface sediments from the central Pacific Ocean (4.5–15ºN, 154–143ºW) was determined using a sequential extraction procedure (SEDEX) to examine the distribution and source of different P species. Total P (TP) concentrations ranged from 13.2 to 119 μmol-P/g with an average of 48.6 ± 27.4 μmol-P/g. Within the TP pool, total inorganic P (TIP) concentrations varied from 11.1 to 121 μmol-P/g, while total organic P (TOP) concentrations ranged from undetectable to 4.8 μmol-P/g. Inorganic P was generally the predominant form in surface sediments, comprising on average up to 93% of sedimentary TP, leaving < 16% as TOP. Among the five P species, the authigenic or $CaCO_3$-bound P and detrital P were the two major P species (comprising on average 43.4 ± 13.5% and 45.7 ± 14.8% of TP, respectively), followed by the refractory organic P, representing 6.7 ± 2.4% of TP. Fe-bound P accounted for 3.3 ± 1.3% of TP, and exchangeable or adsorbed P made up less than 1% of TP. The spatial distribution of different sedimentary P species showed that higher concentrations of detrital P and Fe-bound P were both found at around 11°N, suggesting similar sources for these two P species. Much of the detrital P was derived from atmospheric sources in the study area, where heavy rainfall in the intertropical convergence zone between 3°N and 11°N has been widely reported. Compared with other marine environments, the central Pacific Ocean had relatively higher detrital P, but lower abundance of adsorbed-P and Fe-bound P. These unquine results suggested that most of the labile P could have been released into the water column during its settling from the surface to the seafloor, or that atmospheric inputs of refractory P were an important source for sedimentary P, accounting for an average of 63% of the TP, in the central Pacific Ocean. High proportions of authigenic P in deep-sea sediments, on the other hand, implied that oceanic sediments are an important sink for reactive P species. Relatively lower OC/Org-P and OC/P_{react} ratios suggested a higher sedimentary burial for Org-P and/or attested the importance of detrital P derived from atmospheric sources in the central Pacific Ocean.

1. Introduction

Phosphorus (P) is an important macronutrient for the growth of marine phytoplankton and is thought to control marine productivity over both geological and shorter time scales (Van Cappellen and Ingall, 1996; Tyrrell, 1999; Benitez-Nelson, 2000; Ruttenberg, 2003). Riverine and atmospheric inputs are considered to be the main sources of P to the ocean, and sediments represent an important sink for P in its oceanic biogeochemical cycle (Filippelli, 1997; Delaney, 1998). Phosphorus can be removed from seawater by primary productivity in the euphotic zone and transported to the seafloor and buried in sediments. It can also be removed by various physicochemical processes including adsorption onto particle surfaces such as clay minerals, iron oxyhydroxides, carbonate and the formation of authigenic minerals such as apatite (Eijsink et al., 2000; Zhang and Huang, 2007, 2011) due to the high particle reactivity of P (Lin et al., 2013). Over the last two decades, the SEDEX sequential extraction technique has been widely used to operationally classify sedimentary and suspended particulate P into different phases based on its binding phases and solubility properties (Ruttenberg, 1992; Zhang et al., 2004, 2010) and to study the marine P cycle in the water column and sediments (Ruttenberg and Berner, 1993; Berner and Rao, 1994; Vink et al., 1997; Küster-Heins et al., 2010; Lin et al., 2012, 2013; März et al., 2014). However, studies characterizing P in sediments from open oceans such as the central Pacific Ocean remain few. In addition, previous studies mainly focused on ODP cores and their paleoceanographic significance (Filippelli and Delaney, 1996; Delaney and Anderson, 1997, 2000), but less on spatial distributions and source terms.

The open ocean is the main area for seabed mineral resources and

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could be the potential mineral sources in future (Glover and Smith, 2003; Scott, 2011). Considering its vast area that covers approximately 54% of the earth's surface, and thus large reservoir and inventory for different elements and chemical species including P, the open ocean, both water column and sediments, has received increasing attention, especially on its significance in the global biogeochemical cycles and climatic change (Filippelli and Delaney, 1996; Delaney and Anderson, 1997, 2000; Benitez-Nelson, 2000; Glover and Smith, 2003; Ruttenberg, 2003; Filippelli, 2008). Furthermore, open ocean could also be vulnerable to anthropogenic influences. For example, deep-sea mining of mineral resources, such as polymetallic nodules, could result in the disruption of surface sediments (Glover and Smith, 2003), causing sediments resuspension into the overlying water column. Sequestered P in the sediments would then be released into bottom water, affecting the abundance, distribution, and speciation of P and the benthic ecosystem as a whole.

P is associated with different chemical/physical phases in sediments. Different forms of sedimentary P have different biological and chemical reactivities and thus different geochemical behavior in marine environments (Delaney, 1998; Ruttenberg, 2003; Filippelli, 2008). Therefore, knowledge of chemical speciation of P, in addition to the abundance and distribution of total P, is important for a better understanding of environmental behavior and biogeochemical cycling pathways of P in the ocean. Major P species in sediments include organic P, P associated with hydrous ferric oxides, authigenic carbonate fluorapatite (francolite), hydroxyapatite of skeletal debris, P incorporated in $CaCO_3$, and P adsorbed on other minerals such as clay minerals. Binding forms largely determine whether sedimentary P is reactive or refractory in the ocean (Zhang et al., 2004).

In the present study, we investigated the chemical forms of sedimentary P and their distributions in surface sediments of the central Pacific Ocean. Our objective was to assess the abundance and distribution of sedimentary P and its chemical speciation and sources in the central Pacific Ocean for better understanding the biogeochemical cycle of P in marine environments.

2. Material and methods

2.1. Sampling

Sediment samples were collected from the central Pacific Ocean (4.5–15°N, 154–143°W) during the DY29 cruise onboard the R/V HAIYANGLIUHAO using box-corer in 2013. Our sampling locations were at the west of polymetallic nodules enriched region in the Clarion–Clipperton fracture zone (Fig. 1, Table 1). The box-corer samples represent approximately the top 30–50 cm of the sediment, but only the top 2 cm was used and stored frozen until further processing in the laboratory. Sediment samples were freeze-dried and ground to a fine powder for sieving ($<$200 mesh, 74 μm) with an agate pestle and mortar prior to analysis. Aliquots of the ground sediment samples were taken for the analyses of P using SEDEX sequential extraction, as well as the measurement of total organic carbon (TOC) contents.

2.2. Sequential extraction and measurements

Sedimentary P was chemically fractionated into five operationally defined P species: (1) P adsorbed onto grain surfaces (Adsorbed-P), (2) P associated with easily reducible iron and manganese oxides and/or oxyhydroxides (Fe–P), (3) authigenic carbonate fluorapatite, biogenic apatite and $CaCO_3$-associated P (CFA-P), (4) detrital apatite P (Detr-P), and (5) refractory organic P (Org-P). The specific extraction procedures were largely based on SEDEX sequential extraction technique developed and revised by Ruttenberg (1992) and Zhang et al. (2004, 2010) for marine sediments (Fig. 2).

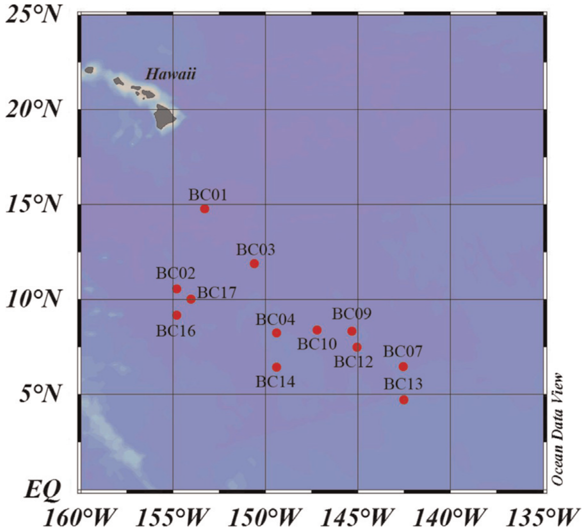

Fig. 1. Sampling locations in the central Pacific Ocean (4.5–15°N, 154–143°W) during 2013.

Extractions were conducted in 50 ml polyethylene centrifuge tubes using about 0.1 g of freeze-dried sediment and 10 ml of the extraction solution. After each extraction, the sample was centrifuged and then the supernatant solution containing the extracted P was analyzed by the standard phosphomolybdenum blue method (Hansen and Koroleff, 1999) on an Agilent 8453 UV–vis spectrophotometer. The same medium as extraction solution for each P species was used to prepare the standard and blank samples. The modified chromogenic reagent was prepared to avoid the interference from extraction solution (e. g., bicarbonate–dithionite extracts of Fe–P) on the phosphomolybdenum blue method (Zhang et al., 2010). Acid extraction solution was neutralized and pre-treated prior to the analysis of phosphomolybdenum blue method. The detection limit for extracted P was 8–10 nM based on replicate blank sample measurements using 5 cm cuvettes, with a precision better than 2%. Reactive P was calculated as the sum of all non-detrital P-phases (P_{react}, Sutula et al., 2004; Lin et al., 2013).

Independent analysis of total sedimentary phosphorus (TP) was also conducted using the high-temperature combustion method (Zhang et al., 2010; Lin et al., 2013) to compare with those from sequential extraction and to ensure data quality. In brief, 0.1 g of sediment sample was wetted with 0.5 M $MgCl_2$ solution and heated in an oven at 95 ºC until dry, followed by ashing in a furnace at 550 ºC for 2 h to decompose organic P compounds. The residue was extracted using 1 M HCl solution at room temperature for about 24 h. Total inorganic phosphorus (TIP) in sediments was directly extracted from sediments with 1 M HCl solution at room temperature for 24 h (Aspila et al., 1976). Both extractions of TP and TIP were quantified after neutralization and dilution. Contents of total organic phosphorus (TOP) were then calculated based on the differences between TP and TIP.

It should be noted that additional filtration was not conducted after sample centrifugation, which might result in potential carryover during the SEDEX extraction procedure. Data of organic fraction in the Adsorbed-P and CFA-P were not presented here due to their extremely low concentrations, typically below the detection limit. Regardless, excellent P recovery also indicated negligible sample loss during our SEDEX extraction procedures (see discussion below) and negligible organic P fraction in the Adsorbed-P and CFA-P phases in the study area.

2.3. Measurement of sedimentary organic carbon

For TOC analysis, about 0.2 g sediment sample was decalcified