

Phosphorus Geochemistry of Marine Records: Examples from Diverse Oceanographic Settings

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In the last few decades, new emphasis has been placed on the importance of nutrients in the ocean, mainly because of their control on productivity and organic carbon burial and, ultimately, on climate. But still little is known about the cycling of biophile elements, such as P, N, Fe etc., their primary source, their fate once in the ocean and in the sediment, and their response to rapid and extreme climate changes.

We concentrate on understanding the geochemistry of phosphorus in marine and non-marine environments, firstly because phosphorus is an essential nutrient controlling and modulating productivity on long time scales, secondly because, due to the lack of an important atmospheric phase and of a substantial input from volcanic and hydrothermal activity, its primary source comes from the continent and its variations in the sedimentary record could be directly linked to changes in continental weathering. The oceanic P balance is therefore controlled by the input from the continent, oceanic circulation, uptake by biomass, transport and regeneration, and finally, burial in a number of different sedimentary sinks (Delaney, 1999).

We have started tracing continent-ocean links in marine Pleistocene sediment records from different regions of the world characterised by diverse oceanographic, climatic, productivity and geographic settings, trying at the same time to seek for feedback mechanisms between climate, productivity and continental weathering, and for glacial-interglacial changes. Samples from ODP sites 658, East equatorial Atlantic; 680, offshore Peru; 724, Arabian Sea, offshore Oman; 798, Japan Sea; 806, Ontong-Java Plateau; 907, North Atlantic Gateways, 1143 and 1144, South China Sea were selected to perform a multi-proxy investigation based on the SEDEX extraction of solid phases of P, mineralogy (by XRD), organic matter determination (by Rock Eval), and nitrogen stable isotopes.

The sequential P extraction allowed to differentiate between reactive and biologically available (Fe-bound P, authigenic P and organic P) and non-reactive (detrital apatite) phosphorus. It is substantial to underline the capability of removing the detrital phase from the total phosphorus budget in the sediments

because of the important implication for the calculation of the C/P ratio and estimates of phosphorus regeneration from organic matter oxidation.

Despite expected differences in the concentration and in the accumulation rates of the 4 extracted P phases between the sites, mainly related to local factors, preliminary results from these studies bring new and interesting insights on the P cycle and possible implications for productivity and climate variations for the last 150,000 years.

In most of the investigated sites detrital P co-varies with other detrital indices, such as quartz and phyllosilicates, and show evident glacial-interglacial variations. Burial of Fe- and organic-bound P, mainly regulated by sedimentation rates and oxygenation near the sediment-water interface, give important indications about chemical conditions in the uppermost part of the sediment. Authigenic P is more and more considered as an efficient and important sink for reactive P and its presence, once thought to be limited to upwelling regions, has been demonstrated in many other sedimentary settings. The precipitation of authigenic P is controlled by many chemical and physical factors, and its variations in the records are interpreted as reflecting important changes in oceanography, input of dissolved P, and regeneration of organic matter. Typical values are about 0.15 mg P/g of sediment for Fe-bound P, ranging between 0.2 and 1.7 mg P/g for authigenic P, with higher values in sediment from the Peru margin, between 0.02 and 0.2 mg P/g for detrital apatite, and between 0.02 and 0.16 mg P/g for organic P.

Against the difficulty of tracing global trends, due to the imprint of regional patterns, mean interglacial values of the phosphorus phases are generally significantly different from glacial values, showing that the burial of phosphorus and its delivery to the oceans are influenced by climate-induced changes.

Delaney ML, *Global Biogeochemical Cycles*, **12**, **4**, 563-572, (1999).