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Phosphorus and iron cycles during early diagenesis of sediments under anoxic water mass in a meromictic Lake Kai-ike

IIDA, Hajime[1*] ; YAMAGUCHI, Kosei E.[2] ; OGURI, Kazumasa[3]

[1]Toho University, [2]Toho University& NASA Astrobiology Institute, [3]JAMSTEC

A meromictic lake Kai-ike is located on the northeastern edge of Kami-koshiki island, Japan. Permanent density stratification develops due to seawater infiltration through a gravel bar separating the lake from the ocean. The oxygenated surface water overlays a stagnant, saline, and anoxic deep water containing hydrogen sulfide. Purple sulfur bacteria (*Chromatium sp.*) inhabit the chemocline at 4.5m depth. At the lake bottom, green sulfur bacteria form microbial mat-like structures (Nakajima et al., 2003). Such environment can be regarded as a model for the past anoxic ocean, such as during Oceanic Anoxic Events (Oguri et al., 2003).

We focused on the early diagenesis of phosphorus and iron in the lake. Phosphorus is a bio-essential element and a limiting nutrient for primary production in the ocean on geological time scales. Biogeochemical processes during early diagenesis in sediments play important roles in controlling oceanic P budget, because P fluxes to and from the sediments depend on redox state of the overlying water. Therefore, it is of great importance to understand early diagenetic geochemical behaviors of P in sediments overlain by, for example, oxic, anoxic, and sulfidic (euxinic) water. In this study, we applied sequential extraction procedures to investigate geochemical behaviors of P and Fe in the surface sediments overlain by sulfidic water of the Lake Kai-ike.

A 25 cm-long KAI4 sediment core (Yamaguchi et al., 2010) was used for two sequential extraction methods. SEDEX method (Ruttenberg, 1992) was used for partitioning phosphorus-bearing species into P_{abs} (absorbed), P_{Fe} (iron-bound), P_{auth} (authigenic), P_{det} (detrital), and P_{org} (organic). Iron-bearing species were also divided into Fe_{HCl} (dissolved in HCl), Fe_{carb} (carbonate), Fe_{ox} (oxide), Fe_{mag} (magnetite), Fe_{py}(pyrite), and Fe_{resi} (residue), following Poulton et al. (2005).

Main phosphorus-bearing form was found to be P_{org}. Its content sharply decreases with increasing depth near the sediment surface. Little precipitation of Fe-hydroxides (no significant peak for P_{Fe} or Fe_{ox}) reflects anoxic water condition. Absence of Fe_{py} at the sediment surface implies that syngenetic pyrite did not form, The Fe_{py} content showed downcore increase as the most abundant Fe-bearing phase.

Transformation of P_{org} and P_{Fe} to P_{auth} is called "sink-switching". At sediment surface in an oxygenated ocean, ferric (oxy)hydroxides precipitate to trap phosphate diffusing from deeper-anoxic sediment, and the phosphate concentration in pore water becomes high enough to precipitate authigenic apatite, meaning effective sink-switching (Slomp et al., 1996).

We compared our results with the previous work focusing on early diagenesis under oxic water mass (Ruttenberg and Berner, 1993). Two differences were clearly observed; the abundant P_{org} with sharp downcore decrease just below the sediment surface, and the similar downcore decrease in P_{tot}. We suggest that the amount of ferric (oxy)hydroxides relative to that of P_{org} (P_{Fe}/P_{org}) is a key factor for the retention of phosphorus in the sediments. Further, we quantified the degree of sink-switching, which appears to be related to P_{Fe}/P_{org} ratio. These results suggest the importance of P_{Fe}/P_{org} for sink-switching as an useful proxy to estimate the extent of benthic phosphorus regeneration.

Very low P_{Fe}/P_{org} ratio or absence of P_{Fe} and Fe_{ox} at the sediment surface reflect anoxic water condition, and further, absence of Fe_{py} and very limited abundance of Fe_{carb} indicate ferruginous condition. Anoxic conditions are also indicated by downcore increase in the Fe_{py} content, Fe_{HR}/Fe_{tot} ratios, and DOP (degree of pyritization; Fe_{py}/(Fe_{py}+Fe_{HCl})) values.

This study provides useful clues for modeling geochemical cycles of phosphorus and iron in the sediments overlain by photic zone anoxia, and for understanding how Fe- and P-related redox proxies recorded early diagenetic processes of the sediments.

Keywords: phosphorus, iron, early diagenesis, photic zone anoxia, anoxic water mass