Phosphorus geochemistry of the central Japan Sea sediments (IODP Exp. 346) 30~220 kyr ago: Implications for the evolution of Asian Monsoon climate system

*Saeka Masuda[1], Kosei E. Yamaguchi[1,3], Satoshi Takahashi[2], Ryuji Tada[2]

1. Chemistry, Department of science, Toho University , 2. Department of Earth and Planetary Science, University of Tokyo, 3. NASA Astrobiology Institute

The Asian monsoon climate system has started about 50 Ma, after the collision of the Indian and Eurasian continents followed by uplift of the Himalaya and Tibetan Plateau. Monsoon influences atmospheric circulation, rainfall, weathering, riverine transport, and ocean currents. It has influenced sediments in the Japan Sea, where occur cm-scale alternation of C_{org}-rich dark and C_{org}-poor light layers. This alternation is most likely due to temporal changes in the nutrient status and/or oceanic redox conditions, which are likely caused by the fluctuations in the intensity of continental weathering and ocean currents, both of which were ultimately caused by the variable monsoon system. In order to obtain insights into the evolving oceanic redox state and the monsoon system, we conducted phosphorus speciation analysis for the drillcore marine sediments recovered by IODP Exp. 346 in the central Japan Sea (e.g., Tada et al., 2015).

Phosphorus, along with nitrogen, is the limiting nutrient for the primary production of the ocean. Supply of phosphorus to the surface ocean is limited to inflow of rivers that contain products of continental weathering. On a long timescale, phosphorus is the most important limiting nutrient for primary production. Phosphate supplied from rivers is taken by organisms in the surface ocean as organic P. More than 99% of the produced organic matter are decomposed and released into the ocean again as inorganic phosphate for recycling. Only some can survive and reach to the ocean bottom.

In an oxic ocean like today, phosphate adsorbs onto precipitating Fe-(oxyhydr)oxide particles. Its fate depends on the redox state of the deep ocean. In an oxic deep ocean, phosphate adsorbed on the Fe-(oxyhydr)oxides reach to the ocean bottom and removed from the ocean. However, if the deep ocean is anoxic, the phosphate-bearing Fe-(oxyhydr)oxides undergo reductive dissolution, where Fe^{2+} and PO_4^{3-} are released into the waterbody. If the deep ocean is euxinic (i.e., stagnant, anoxic, and sulfidic), the released Fe^{2+} combines with sulfide formed by activity of sulfate-reducing bacteria, and phosphate would form carbonate fluoroapatite (CFAP) with carbonate ions produced upon decomposition of organic matter during bacterial sulfate reduction. The CFAP is highly insoluble and preserved in sediments.

In order to explore changes in the nutrient status and redox conditions that were influenced by Asian monsoon, we investigated phosphorus speciation in the marine sediments recovered in 2013 in the central (core U1423) and northeastern (core U1425) parts of the Japan Sea by IODP Exp. 346. The samples were quantified for five P-bearing species (P_{abs}, P_{Fe}, P_{auth}, P_{det} and P_{org}) by modified SEDEX method of Ruttenberg (1992) and Ruttenberg et al. (2009).

The most abundant P-bearing species is P_{auth} (Ave. 0.044 wt.%), followed by P_{org} (Ave. 0.016 wt.%) that show negative correlation with P_{auth} contents (at U1423). The least abundant species is P_{abs} (Ave. 0.004 wt.%). These results suggest that organic matter produced in the surface ocean was decomposed to release phosphate, which eventually formed authigenic apatite in the sediments, implying that the ocean was oxic and/or biological activity was enhanced. These results are consistent with Ce/Ce* values as a proxy of oceanic redox condition. Furthermore, layers rich in phophorus are mostly dark in color, suggesting active summer monsoon; increased rainfall in east Asian regions promoted continental weathering and riverine input (by the Yangtze River) of nutrients like phosphorus, which flow through the

Tsushima Current and entered into the Japan Sea.
Using the same core samples used in this study, sulfur speciation and isotope analyses have been done and will be reported elsewhere. Iron speciation analysis is being done. Much more work is obviously necessary to better constrain the past nutrient status and redox conditions in the Japan Sea that were influenced by the evolving Asian monsoon system.

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