

Phosphorus speciation analysis of sediments in the hypersaline Meedee Lake, off Crete Island, Eastern Mediterranean Sea

Yurie Yamaguchi^{1*}, Kosei E. Yamaguchi², Masafumi MURAYAMA³, Minoru Ikehara³

¹Department of Chemistry, Graduate School of Science, Toho University, ²Department of Chemistry, Graduate School of Science, Toho University, Nasa Astrobiology Institute, ³Center for Advanced Marine Core Research, Kochi University

Submarine, hypersaline lakes have been found off Crete Island, Eastern Mediterranean Sea. Among them, "Meedee Lake" has a unique environment where its salinity is more than 10 times higher than that of normal seawater, due to elution of submarine evaporites formed during Messinian Salinity Crisis (MSC) 5.33 to 6 Ma ago. The lake water has been kept essentially anoxic due to consumption of dissolved oxygen by decomposition of organic matter in a density-stratified lake. In order to understand changing redox state, environments, and microbial activity in the lake, sediments core was collected by KH06-04 cruise. The sediments show alternation of light- and dark-colored layers. Reflecting fluctuating redox state during deposition (Izumitani, 2010).

Phosphorus is one of the bio-essential elements for life on earth and plays an important role in regulating biological productivity in oceans and on continents (Van Cappelen and Ingall, 1994, 1996). Influenced by microbial activity, redox state, and diagenesis, P exists as various forms in marine sediments. Thus, P speciation could be an important clue for better understanding of sedimentary environments. We applied phosphorus speciation analysis for the sediments to quantify transition of redox sensitivity.

Five sedimentary P reservoirs were separately quantified: (1) loosely sorbed P+biogenic apatite+CaCO₃-associated P, (2) Fe-bound P, (3) authigenic carbonate fluorapatite (CFAP). (4) Detrital apatite P, by using five-steps sequential extraction technique following the method of Hashimoto (2010), based on Ruttenberg (1992) and Schenau and de Lange (2000). Molybdenum blue method was applied to determine P concentration by using a UV-VIS spectrophotometer.

CFAP concentration was much higher than other forms, accounting for 76% of light colored layers and 67% of dark colored layers. Concentration of organic P (Porg) and detrital apatite P (Pdet) were much lower than expected. The largest concentration differences between light- and dark-colored layers were Fe-bound P (PFe), and its concentration decreases with sediment lightness. possibly, reflecting transition of redox state. Under anoxic condition, phosphate was released from Fe-(oxyhydr)oxides during their reductive dissolution, indicating deposition of light-colored layer under anoxic condition and dark-colored layer under oxic condition. This suggestion is consistent with the results of Izumitani (2010).

Generally, abundance of organic matter in surface sediments decreases with increasing concentration of oxygen in porewater and overlying water. Then Porg content is expected to decrease; however, an opposite result was obtained. This discrepancy was probably caused by either of following factors. First, sinking particles of organic matter may have some difficulty in penetrating the hypersaline dense lake water. Furthermore, benthic foraminifera was relatively large in number and high in diversity in dark-colored layers (Izumitani, 2010). Therefore, the origin of Porg in dark-colored layers may possibly be benthic foraminifera. Second, influence of climate change may have some effects on the sedimentary environment of the saline lake. Izumitani (2010) suggested that, using the same core, the light-colored layers deposited in interglacial periods and the dark-colored layers in glacial periods. Deposition of organic matter was enhanced in the glacial periods because of increasing biological productivity during eutrophication in ice-covered ocean.

CaCO₃-associated P concentration would be the largest where foraminifera are abundant, but CFAP concentration was much higher than the other P-bearing forms. This is probably because changing decomposition rate of phosphorus in Meedee Lake led PFe and Porg to alternate with CFAP, or because CFAP concentration reflects concentration of abiotically-formed CaCO₃ derived from evaporite minerals formed during MSC.