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Hypoxia in the water column expedites Mn-carbonate precipitation in manganese-rich coastal sediments in Jinhae Bay, Korea

JUNG-HO HYUN[1], JIN-SOOK MOK[1], YOUNGHOON WON[2], SANGBEOM BAEK[1] AND GIEHYEON LEE[2]

[1]Hanyang University

[2]Yonsei University

Presenting Author: hyunjh@hanyang.ac.kr

The carbon buried in continental margins including coastal ocean comprises 20% (455 PgC) of the carbon in entire marine sediments. Therefore, it is particularly important to understand the process controlling the dynamics (i.e., precipitation or release) of carbon in organic-rich coastal sediments to evaluate the role of coastal sediments as a carbon reservoir in ocean environments affected by climate change and human activities. More than 500 sites in coastal ocean have reported hypoxic condition with oxygen concentrations less than 2 mg L^{-1} (63 μmol L^{-1}). Under the hypoxic conditions, anaerobic microbial processes such as the reduction of manganese, iron and sulfate become dominant organic carbon (C_{org}) mineralization pathways, which greatly alters biogeochemical cycles of C-Mn-Fe-S at the sediment-water interface. We investigated the impact of water column hypoxia on the C_{org} mineralization by manganese reduction and precipitation of manganese carbonates in the sediments of the Jinhae Bay, characterized by high manganese content (> 50 μmol cm^{-3}). Sediments were collected 4 times according to the hypoxic conditions of the water column (i.e., pre-hypoxia, early-hypoxia, late-hypoxia and post-hypoxia). Total manganese was enriched in surface sediments in pre-hypoxia condition. During the early-hypoxia, manganese reduction dominated C_{org} mineralization, which generated dissolved manganese (Mn^{2+}) and dissolved inorganic carbon. In late-hypoxia, sulfate reduction dominated C_{org} mineralization, and Mn^{2+} decreased as the sulfide reacts with Mn^{2+} to form MnS. During the post-hypoxia, both dissolved and solid phase manganese were depleted in sediments as the manganese is released into the overlying water column. XANES (X-ray Absorption Near Edge Structure) analysis revealed that the precipitation of manganese carbonate ($MnCO_3$, rhodochrosite) increased from 4% of total solid Mn in pre-hypoxia to 10% and 20% of the total Mn in early- and late-hypoxia condition, respectively. Our results implied that the burial (sequestration) of carbonate minerals in coastal sediments is closely related to the development of hypoxia in water column. Considering the significant amounts of C_{org} buried in coastal sediment and the expansion of hypoxia in coastal ocean, it is significant to quantify the formation of carbonate minerals (i.e., $MnCO_3$, $FeCO_3$ and $CaCO_3$) in coastal sediments associated with the hypoxia in water column.