Influence of manganese on the behavior of cobalt in the East China Sea

*Kuo Hong Wong[1,2], Jiarui Xu[2], Idha Yulia Ikhsani[2,3], Ronald Muhammad[2], Taejin Kim[4], Asami Mashio[1], Hiroshi Hasegawa[1], Hajime Obata[2]

1. Kanazawa University, 2. Atmosphere and Ocean Research Institute, The University of Tokyo, 3. Research Center for Deep Sea, Indonesia Institute of Sciences, 4. Pukyong National University

Background

Mn and Co are important micronutrients for phytoplankton. Co is the metal center of the biologically essential vitamin B_{12}, while Mn is involved in photosynthesis. Coastal regions are major sources of Mn and Co, which are then transported into the open ocean. However, both Mn and Co have short residence times in seawater. This is because dissolved Mn(II) oxidizes rapidly to particulate Mn(III) or Mn(IV) oxides under oxic condition. Bacteria that catalyze the oxidation of Mn also co-precipitate Co(II) onto particulate Mn oxides, thus removing Mn and Co simultaneously from the dissolved phase. Therefore, the oxidation of Mn may affect the biogeochemical cycling of Co in Mn-rich coastal regions. This study aims to reveal the major sources of Mn and Co and elucidate the influence of Mn oxidation on the behavior of Co in the East China Sea (ECS), where wide continental shelf, complex topography, and unique water mass movements control the distributions of trace metals.

Methods

Mn concentrations in the samples were determined using ICP-MS (NexION 2000, Perkin Elmer or Element XR, Thermo Fisher) following pre-concentration by chelating resin (NOBIAS PA-1). Before analysis, the seawater samples (pH = 2.0) were adjusted to pH 6.0 using NH_3 solution and NH_4Ac buffer. The chelating resins were first washed using 10 mL of acetone and 5 mL of 2 M HNO_3, then conditioned to pH 6.0 using NH_4Ac buffer. Mn was extracted by passing the samples through the chelating resin column and was eluted using 2 M HNO_3.

Co concentrations in some samples were determined similarly to Mn, using pre-concentration by chelating resin followed by analysis using ICP-MS, while the remaining samples were analyzed by cathodic stripping voltammetry. Prior to analyses, UV-irradiation was used to destroy natural organic ligands in the samples. In the voltammetry method, seawater samples were adjusted to pH 9.0 using NH_3 solution and NH_4Cl buffer. An artificial ligand, nioxime, was then added into the solution before analysis.

Results and Discussion

In the surface waters of the ECS, Mn and Co concentrations were high but there were no observable losses of Mn and Co due to oxidation. The strong negative correlation between Mn and Co with salinity (R^2 = 0.91 and 0.94, respectively) indicated that the main source of both metals was the Yangtze River, the largest freshwater source in the region. The persistence of Mn and Co in the surface waters could be ascribed to the rapid photoreduction of Mn oxides because the lack of Mn oxide formation also prevented the removal of Co. In addition, the surface waters of the ECS are rich in dissolved organic matter derived from terrestrial or biological sources. Hence, Mn and Co may exist as organic complexes that are resistant to bacterial oxidation.

In the intermediate waters beyond the continental shelf, Co had strong positive correlation with phosphate (R^2 = 0.92; Co/PO_4 = 17 μmol mol^{-1}), which was observed at 200-1000 m depth in the subtropical North Pacific but only at 200-500 m along the Kuroshio waters. The Kuroshio waters had significantly lower Co/PO_4 ratios and higher Mn concentrations at around 700 m, suggesting removal of Co by Mn oxidation. At this depth, a sill blocked the movement of intermediate waters into the ECS and caused resuspension of Mn from surface sediments. Chemical speciation analysis also showed that the Co

complexing capacities of organic ligands in the intermediate waters were relatively low and thus unlikely to prevent co-oxidation of Co with Mn.
In the eastern ECS, the Okinawa Trough has intense hydrothermal activities that resulted in significant increases in Mn concentration. However, there were no changes in Co concentrations. The difference in the behaviors of Mn and Co may be attributed to the following reasons: (1) the hydrothermal vents of Okinawa Trough are not major Co suppliers, or (2) very high concentrations of Mn instantaneously co-precipitated with hydrothermal-derived Co.

Keywords: Manganese, Cobalt, East China Sea, Okinawa Trough, Kuroshio, Yangtze River

