Dissolved zinc and its speciation in the Tachibana Bay, Nagasaki

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Introduction
Zinc (Zn) is an essential micronutrient for bacteria and phytoplankton in the ocean. Laboratory studies examining the influence of Zn on phytoplankton growth showed that coastal species could be zinc-limited (Bruland et al., 1983). Reportedly, organic complexes of dissolved zinc in surface waters account for about 98% of the total dissolved zinc, which reduces the bioavailable fraction of zinc, the free metal ion (Zn²⁺), to a level as low as 1 pmol/L (Bruland et al., 1991). Therefore, Zn speciation is important to understand biogeochemical cycles of Zn in the ocean. In this study, by using cathodic striping voltammetry (CSV), distributions of dissolved Zn and its speciation were determined to investigate the geochemical processes of Zn in the Tachibana Bay, where active hydrothermal activity was reported at the coastal area.

Methods
Seawater samples from surface to near bottom (D=36 m) were collected in the Tachibana Bay, Nagasaki Prefecture by using acid-cleaned X-type Niskin samplers during TS Kakuyo-maru cruise (May 2012). All of seawater samples were filtered with capsule filters (<0.2µm, Acropak). After filtration, sulfide in seawater was determined onboard by using CSV. Samples for total dissolved Zn (CZn) were acidified to pH<1.8 with ultra pure HCl and samples for Zn speciation were frozen immediately onboard ship. On a land-based laboratory, total dissolved Zn were determined by using CSV after UV-digestion. For the Zn speciation, ligand concentrations (CL) and conditional stability constants (K’ZnL) were obtained from a titration using competitive ligand equilibrium / adsorptive cathodic striping voltammetry (Van den Berg, 1985).

Results and Discussion
In the Tachibana Bay, total dissolved Zn (CZn) was ranged from 0.33 to 3.1 nM, which were similar concentration level compared to those in the open ocean. CZn was sharply decreased at the bottom compared to the near the surface. High sulfide concentration (90 nM) was observed near the bottom, reflecting active hydrothermal system near the bottom of Tachibana Bay. Zn is seemingly removed as Zn-sulfides from the water column. Also, relatively high total ligand concentration (CL) was calculated near the bottom. The biogeochemical cycling of Zn in the Tachibana Bay is considerably affected by hydrothermal system.

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