# Organic complexation of zinc at the shallow hydrothermally active area of the Tachibana Bay, Nagasaki

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## I. Introduction

Trace metals, like Zn, are used in numerous enzyme systems involved with a variety of metabolic processes. Low Zn concentrations in surface seawater could limit growth of some kinds of phytoplankton (Brand et al., 1983; Sunda and Huntsman, 2000). Therefore, it is an important subject to reveal the biogeochemical cycles of Zn in the ocean.

Recently, dissolved Zn enrichments near the hydrothermal vents have also been observed in the Mid-Atlantic Ridge and East Pacific Rise (Conway and John, 2014; Roshan et al., 2016), which suggested mantle-derived Zn from the hydrothermal vents could be a major source of dissolved Zn in ocean environment (Roshan et al., 2016). Sander and Koschinsky (2011) mentioned that organic ligands could potentially stabilize dissolved Zn in hydrothermal fluids and plumes. However, this process in the hydrothermal system has not been investigated enough yet.

In this study, we determined dissolved trace metal (Mn, Fe, Cu, and Zn) concentrations, Zn organic speciation, and dissolved sulfide in seawater in Tachibana Bay near the coast of Obama hot springs.

## II. Sampling and Methods

Seawater samples were collected using acid-cleaned samplers with external springs mounted on CTD-CMS system during a research cruise KY-340 of TS *Kakuyo-maru*, May 2012. The samples were collected in low-density polyethylene bottles through a 0.2 μm-pore size filter. Samples for dissolved trace metal analysis were acidified to a pH of less than 1.8 using ultrapure HCl, and stored. Another set of samples, for Zn speciation analysis, was frozen at -18°C immediately after sampling. The samples were brought back to the laboratory and analyzed using CLE-CSV for Zn speciation (Kim et al., 2015), and using ICP-MS for trace metal concentrations (Kondo et al., 2016).

## III. Results and Discussion

The ranges of dissolved Mn (13.3 –39.3 nM), dissolved Fe (1.8 –16.5 nM), and dissolved Cu (1.8 –2.6 nM) in seawaters of Tachibana Bay were within the concentration levels in the East China Sea. The dissolved Zn concentrations ranged from 0.3 to 3.1 nM, which were also similar concentration level to those in the East China Sea.

Vertical distributions of dissolved trace metals (Mn, Fe, Cu, and Zn) at the coastal hydrothermal area showed different features compared to those at the center of Tachibana Bay. At the coastal area, dissolved Mn and Fe concentrations were generally high and increased toward the bottom, whereas dissolved Cu and Zn concentrations were decreased. On the other hand, vertical distributions of trace metals at the center of the bay were relatively constant. We discuss the role of organic complexing ligands and sulfide on Zn and Cu distributions in the coastal hydrothermal environment.

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