

Distribution and speciation of copper in seawater of East China Sea and its surrounding areas

*Kuo Hong Wong¹, Hajime Obata¹, Toshitaka Gamo¹

1. Atmosphere and Ocean Research Institute, The University of Tokyo

I. Introduction

Copper is an essential micronutrient for all living organisms as it plays an important role in electron transfer in many life-supporting systems, and is present in many enzymes and proteins. However, at high concentrations in seawater, Cu^{2+} is known to be toxic to marine microorganism. Therefore, many phytoplankton and bacterial species have the ability to release Cu-complexing ligands to decrease the concentration of Cu^{2+} and reduce its toxicity. As a result, at the eutrophic surface waters, more than 99% of Cu are complexed with organic ligands. Hence, in this study, we determined the total dissolved Cu concentrations, Cu speciation parameters and Cu^{2+} concentrations at 15 stations in the East China Sea and its surrounding areas.

II. Sampling and Methods

Seawater samples were collected using acid-cleaned, Teflon-coated X-type Niskin samplers mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS) onboard R/V Shinsei Maru during KS-15-6 cruise (June-July 2015) and R/V Hakuho Maru during KH-15-3 cruise (October 2015). The samples were collected in low-density polyethylene bottles through a 0.2 μm -pore size filter. Samples for total Cu analysis were acidified to a pH of less than 1.8 using ultrapure HCl, and stored. Another set of samples, for CLE/CSV analysis, was frozen at -18°C immediately after sampling. The samples were brought back to the laboratory and analyzed using CLE-CSV with salicylaldoxime (SA) as the competing ligand (Campos and van den Berg, 1994).

Samples used for total dissolved Cu were placed under UV radiation for 60 minutes to destroy all organic ligands prior to analysis. Frozen samples for Cu speciation analysis were allowed to thaw for 24 hours at 4°C , and then placed at room temperature for 4-8 hours. 10mL of sample, borate buffer, and a known concentration of Cu were added into two sets of 10 Teflon vials, left for at least 2 hours to allow the natural ligands to equilibrate with the added Cu, and the competing ligand, SA, was then added into the solution. The vials were then left to equilibrate overnight before analysis. 5 μM SA and 1 μM SA were used as the competing ligand for each of the two titrations, respectively.

III. Results and Discussion

The highest concentration of total dissolved Cu was found at the surface (10m) of Stn.05, where $[\text{Cu}] = 4.65\text{nM}$ and the lowest concentration was at Stn.13 ($[\text{Cu}] = 0.47\text{ nM}$ at 100m). Surface waters at Stn.03, Stn.04 and Stn.05 have relatively low salinities when compared to those of other stations, and this can be attributed to the freshwater discharge from Yangtze River, which is likely a major source of copper into the East China Sea (Koshikawa et al., 2007; Abe et al., 2003). Two classes of ligands were found in the surface waters in this study. The concentration of the stronger ligand, L_1 , ranged from 0.63 nM to 6.11 nM, with an average log K value of around 14, whereas for the weaker ligand, L_2 , the concentrations were in the range of 4 nM to 27 nM, with an average log K value of around 12.3. Cu^{2+} concentrations remain constant at all stations ($\sim 10^{-14}\text{ M}$) despite the large fluctuations in total Cu concentrations. The large ligand pool had probably buffered against changes in Cu concentration in seawater.

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Keywords: Copper, Speciation, East China Sea

The Translocation and Remediation of Thallium and Chromium by River System after Pollution

*Lijie Han^{1,2}, Shenghong Hu², Dong Huang¹, Mingming Zhang¹, Yaping Qin¹

1. Analytical Lab, the fifth geological team, 2. State Key Laboratory of Biogeochemistry and Environmental Geology, China University of Geosciences

Heavy metal pollution of water system has been and still is the most serious environmental in most country especially development country. In 2013, the West river and He river system have accidentally polluted by large amount of wastewater containing high amount of thallium and chromium. Right after the accident, we collected and analyzed more than 2000 water samples around the accident site and downstream of the river to assess the scope of the pollution. We also collected and analyzed many sediment samples from river bed to evaluate the translocating of those heavy metal. In this report, we first discussed the analytical techniques and sample preparation methods for the analysis. Furthermore, we correlated the determined content of Tl and Cr from those collected water samples with the distance of sample collecting sites from the pollution source site, and discussed the spatial migration. We also correlated the the Tl and Cr content with the collection time of those water samples and discussed the translocation on time base. At last, by comparing the data from water and sediment samples, we further discussed the translocating rate (in both time and quantity scale) of these two pollution metals between different matrix. Those results will provide significant impact and insight on studying spontaneous remediation, and the translocation/absorption of pollution by large river.

Keywords: Thallium and chromium, River pollution, Remediation, Dynamic translocation

Towards high-precision Pb-Pb dating of extra-terrestrial materials by MC-ICPMS

*Ito Kengo¹, Tsuyoshi Iizuka¹

1. The university of Tokyo

Knowledge of the timescales of condensation of the first solids from the solar nebula, accretion, differentiation and metamorphism of asteroids is essential to decode the early evolution of our solar system. Considering the possible overall time spans from molecular cloud to planetary systems of ~10 Ma, and much shorter timescales of individual events, a high-precision age determination (error ± 0.1 Ma) is required. The U-Pb system offers such high-precision chronometer because of having two decay chains. In this study, we have evaluated the precision and accuracy of Pb isotope analysis by multiple collector-inductively coupled plasma mass spectrometry (MC-ICPMS). The MC-ICPMS has advantages in simple usage and high analytical throughput compared with TIMS which is the conventional method to measure Pb isotope ratio. We applied two independent mass-bias correction methods for Pb isotope ratio measurements of synthetic Pb solution: external-normalization by doping Tl standard and internal-normalization by adding ^{202}Pb - ^{205}Pb double spike. We found that there is no remarkable difference in the analytical accuracy between the two methods. We also found that a precision of 0.01% can be achieved for isotope analysis of ~100 pg of Pb.

Taking another view of high precision and accuracy Pb dating, removal of non-radiogenic Pb is important before isotopic analysis and this can be achieved by acid leaching. For establishing a robust leaching method, it is important to understand what minerals and elements are eluted in multiple leaching steps. This has been investigated by combining SEM imaging of acid-washed samples and chemical analysis of leachates.

Keywords: the early solar system, Pb-Pb dating, ICPMS

High-precision multipoint radiocarbon dating and reconstruction of the eruption history of the Mt. Fuji during the last 8,000 years using sediment cores obtained from the Fuji Five Lakes

*Gen Nagano¹, Yusuke Yokoyama¹, Stephen Obrochta², Yosuke Miyairi¹, Mitsuhiro Yoshimoto³, Shinya Yamamoto³

1. Atmosphere and Ocean Research Institute, University of Tokyo, 2. Faculty of International Resource Sciences, Akita University, 3. Mount Fuji Research Institute, Yamanashi Prefectural Government

Mt. Fuji is an active volcano, located at the plate boundary of the Philippine Sea plate, the Eurasia plate and the North American plate, with the continuous activity characterized by basaltic magma from about 100,000 years ago. Drilling on land has been conducted repeatedly to reconstruct the eruption history through the stratigraphy of the volcanic product. However, there are only a few studies on lake sediments of the Fuji Five Lakes, especially Lakes Motosu and Sai and the sedimentary environment is less understood. Here we present the sedimentary stratigraphy using X-ray fluorescence core-scanner analysis in Lake Motosu and Sai, combined with the high-resolved radiocarbon dates of bulk sediments (109 samples) and plant fossils (20 samples) using accelerator mass spectrometry to reconstruct the eruption history of Mt. Fuji.

The radiocarbon dates of bulk sediments and plant fossils indicates the continuous sedimentary environment during the last 8000 year. A high-resolved age model was constructed in Lake Motosu and the validity of the age model was evaluated by Kawagodaira Pumice (3149 ± 12 cal yBP ;Tani et al., 2013). The number of scoria layers in cores was more than previous works on land, suggesting that the analysis of lake sediments could detect small eruptions. Moreover, the analysis of organic matter properties (total organic carbon, total nitrogen, total sulfur content and C / N ratio) indicates the change in supply of organic matters from the lake catchment. We concluded that the analysis of the lake sediments near the volcano is useful for clarifying the history of volcanic eruption, as well as paleoclimate change.

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Keywords: Mt. Fuji, Radiocarbon dating, Eruptive history, Age model