

Seasonal change of Iron species and concentration of soluble Iron in the atmosphere in Northwest Pacific region based on the analysis of aerosols collected in Tsukuba, Japan

Y. TAKAHASHI* AND T. FURUKAWA

Hiroshima University, Hiroshima 739-8526, Japan

(*correspondence: ytakaha@hiroshima-u.ac.jp)

Atmospheric iron (Fe) can be a significant source of nutrient for phytoplankton in remote ocean, which in turn has a large influence on Earth's climate. Whether Fe in aerosol can be a bioavailable or not depends mainly on the soluble fraction of Fe. However, factors controlling the soluble fraction of Fe have not been understood fully, since there can be many factors controlling the fraction. In this study, Fe species, chemical composition, and soluble Fe concentration in aerosol collected at Tsukuba through a year were investigated to identify the factors controlling the amount of soluble Fe supplied into ocean. The concentration of soluble Fe in aerosol is correlated with those of sulfate and oxalate which originate from anthropogenic sources, suggesting that soluble Fe is mainly derived from anthropogenic sources. Moreover, the concentration of soluble Fe (%) is also correlated with enrichment factors (EF) of vanadium (V) and nickel (Ni) emitted by fossil fuel combustion. These results suggested that the degree of Fe dissolution is controlled by the magnitude of anthropogenic activity such as fossil fuel combustion. In addition, XAFS was performed in this study to identify the Fe species in aerosols. The fitting of XAFS spectra coupled with micro-XRF showed that main Fe species in aerosols in Tsukuba were illite, ferrihydrite, hornblende, and Fe(III) sulfate. Moreover, soluble Fe fraction to total Fe in each sample measured by leaching experiment is closely correlated with the Fe(III) sulfate fraction determined by XAFS, suggesting that the presence of Fe(III) sulfate is primarily important for the supply of soluble Fe into the ocean. Another possible factor, total concentration of Fe(III) in the atmosphere in terms of the amount of supply of soluble Fe into ocean was high in spring due to the high concentrations of mineral dust in the period in East Asia, but this factor does not contribute to the amount of soluble Fe to a larger degree than the effect of Fe(III) sulfate. Thus, it was concluded that the most significant factor controlling the supply of soluble Fe in North Pacific can be the concentration of anthropogenic Fe species such as Fe(III) sulfate.

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[2] Y. Takahashi *et al.*, *Atmos. Chem. Phys. Discuss.* 13 (2013) 7599.

Vertical profiles of copper isotopic composition in the ocean

SHOTARO TAKANO¹, MASAHARU TANIMIZU²,
TAKAFUMI HIRATA³ AND YOSHIKI SOHRIN¹

¹Institute for Chemical Research, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan (Correspondence: shotaro@inter3.kuicr.kyoto-u.ac.jp)

²Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology, 200 Monobe Otsu, Nankoku 783-8502, Japan

³Division of Earth and Planetary Sciences, Kyoto University, Kitashirakawa Oiwake-cho, Kyoto 606-8502, Japan

Copper is an essential trace metal that shows a vertical recycled-scavenged profile in the ocean. To elucidate the biogeochemical cycling of Cu in the oceans, it is important to determine the profiles of Cu isotopes in the ocean. However, precise isotopic analysis of Cu has been impaired by the low concentrations of Cu as well as co-existing elements that interfere with measurements by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). We have developed a precise and simple method for determining the isotope composition of dissolved Cu in seawater¹. Dissolved Cu was preconcentrated using a Nobias Chelate-PA1 resin and purified using an AG MP-1 anion exchange resin. The concentration and isotopic composition of copper were measured using an Element 2 HR-ICP-MS and a Neptune MC-ICP-MS, respectively. Cu isotopic composition data were expressed as $\delta^{65}\text{Cu}$, where $\delta^{65}\text{Cu}$ (‰) = $[(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}} / (^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST SRM 976}} - 1] \times 10^3$.

We have determined $\delta^{65}\text{Cu}$ in the western North Pacific and Japan Sea. In the western North Pacific, $\delta^{65}\text{Cu}$ values were +0.45–0.53‰ above the thermocline. Below the thermocline, $\delta^{65}\text{Cu}$ values were increased to +0.49–0.71‰. In the Japan Sea, $\delta^{65}\text{Cu}$ values were +0.48–0.57‰ above the thermocline, which were similar to that of the western North Pacific. Below the thermocline, however, $\delta^{65}\text{Cu}$ values were lighter (+0.28–0.56‰) than that of the western North Pacific. We will also reveal the distribution of $\delta^{65}\text{Cu}$ in the eastern North Pacific and central Indian Ocean. We are going to constrain biogeochemical cycles of Cu using $\delta^{65}\text{Cu}$ and Cu concentration data. Our hypotheses at present is that $\delta^{65}\text{Cu}$ above the thermocline is balanced by biological removal of light Cu and aeolian supply of light Cu, and that $\delta^{65}\text{Cu}$ below the thermocline become heavy with the increase in AOU because of preferential removal of light Cu.

[1] Takano, S., Tanimizu, M., Hirata, T., Sohrin, Y., submitted. (2013) *Anal. Chim. Acta*.