

## Detection of low isotopic ratio of iron in anthropogenic aerosols and evaluation of its contribution to the ocean

KURISU, Minako<sup>1\*</sup>; IIZUKA, Tsuyoshi<sup>1</sup>; MIYAHARA, Aya<sup>2</sup>; YAMAKAWA, Yoshiaki<sup>1</sup>; MIYAMOTO, Chihiro<sup>1</sup>; SAKATA, Kohei<sup>2</sup>; SAKAGUCHI, Aya<sup>3</sup>; TAKAHASHI, Yoshio<sup>1</sup>

<sup>1</sup>Graduate School of Science, The University of Tokyo, <sup>2</sup>Graduate School of Science, Hiroshima University, <sup>3</sup>Faculty of Pure and Applied Sciences, University of Tsukuba

Productivity of phytoplankton affects global carbon cycle, and may also affect the climate. Iron (Fe) is an essential element for phytoplankton, but its solubility is low and much of it is removed as Fe (III) hydroxide. Therefore, it has been reported that phytoplankton growth in the High Nutrient-Low Chlorophyll (HNLC) regions is limited by Fe concentration (Martin and Fitzwater, 1988). Aerosols are important sources of Fe species to the surface seawater. They are classified into anthropogenic and natural ones. Particle sizes of anthropogenic aerosols are generally smaller than those of natural ones because of their different formation processes (Whitby, 1977). Previous studies have shown that high soluble Fe species were included in anthropogenic aerosols (e.g., Takahashi et al., 2013). In terms of Fe isotope composition, Mead et al. (2013) compared Fe isotopic compositions between coarse aerosols ( $> 2.5 \mu\text{m}$ ) and fine ones ( $< 2.5 \mu\text{m}$ ) and suggested that the Fe isotopic composition of finer aerosols (anthropogenic source;  $\delta^{56}\text{Fe} = -0.10 \text{‰}$ ) is lighter than that of coarse aerosols (natural source;  $\delta^{56}\text{Fe} = 0.08 \text{‰}$ ). However, it is possible that the separation of the aerosols at the particle size of  $2.5 \mu\text{m}$  cannot fully separate the two sources. The purpose of this study, therefore, was to detect anthropogenic aerosols and measure their Fe iron isotopic compositions. Size-fractionated aerosol samples were collected at Higashi-Hiroshima City using a cascade impactor (particle sizes:  $> 10.2 \mu\text{m}$ ,  $4.2 \sim 10.2 \mu\text{m}$ ,  $2.1 \sim 4.2 \mu\text{m}$ ,  $1.3 \sim 2.1 \mu\text{m}$ ,  $0.69 \sim 1.3 \mu\text{m}$ ,  $0.39 \sim 0.69 \mu\text{m}$ ,  $< 0.39 \mu\text{m}$ ), which could specify the isotopic compositions of anthropogenic Fe. Iron isotopic compositions of bulk aerosols and soluble aerosols for simulated rain water were measured using multi-collector inductivity-coupled plasma mass spectrometry (MC-ICP-MS; Neptune Plus, Thermo Scientific). The chemical species were also identified by employing Fe K-edge X-ray absorption fine structure (XAFS) spectroscopy and their solubility for seawater was evaluated by leaching experiments. As a result, Fe isotopic compositions ( $\delta^{56}\text{Fe}$ ) of larger particles were around  $+0.25 \text{‰}$ , whereas smaller particles showed lower isotopic composition ( $-0.5 \sim -2 \text{‰}$ ). In addition, smaller particles of soluble component for simulated rain water showed much lower  $\delta^{56}\text{Fe}$  values ( $\delta^{56}\text{Fe} = -3.9 \text{‰}$ ) than bulk particles, suggesting that anthropogenic Fe has much lower isotopic compositions. The value was the lowest among other environmental samples reported so far. This means that the large isotopic fractionation of anthropogenic aerosols occurs when Fe species evaporate.  $\delta^{56}\text{Fe}$  value of the remaining materials after the water-extraction experiment was calculated using the values of bulk Fe and soluble Fe, and it was revealed to be similar to that of earth's crust ( $+0.25 \text{‰}$ ). This means that the anthropogenic Fe in aerosol is completely soluble and has very low  $\delta^{56}\text{Fe}$ . It has been suggested that Fe in aerosol contributed significantly to the supply of Fe in surface seawater. When considering Fe isotopic budget for surface seawater using the value measured in this study as a  $\delta^{56}\text{Fe}$  of anthropogenic aerosol ( $-3.9 \text{‰}$ ), it is suggested that aerosols is main source of Fe dissolved in the surface seawater.

Keywords: iron isotopic composition, aerosol, anthropogenic iron