

## Speciation and stable isotope study for iron in aerosols from various sources to determine their contributions to HNLC region

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In the North Pacific, three sources of iron (Fe) transported via atmosphere can be suggested: (a) mineral dust from East Asia, (b) anthropogenic Fe, and (c) aerosols from volcanic origin. Considering these different sources, Fe can be found and transported in a variety of chemical forms, both water-soluble and -insoluble. It is generally believed that only the soluble fraction of Fe can be considered as bioavailable for phytoplankton. To assess the biogeochemical impact of the atmospheric input, attempt was made to determine Fe species by X-ray absorption fine structure spectroscopy (XAFS) and its water solubility, in particular to compare the three sources. In particular, it was found that Fe stable isotope contribute to determination of Fe emitted from anthropogenic sources.

(i) Iron species and soluble Fe content in aerosol collected at Tsukuba (Japan) through a year were investigated to compare the contributions of mineral dust and anthropogenic components. It was found that the soluble Fe content is correlated with those of sulfate and oxalate originated from anthropogenic sources, suggesting that soluble Fe is mainly derived from anthropogenic sources, which was supported by XAS analysis showing presence of Fe(III) sulfate. Moreover, soluble Fe content was closely correlated with that of Fe(III) sulfate. In spite of supply of high concentrations of Fe in mineral dust from East Asia, anthropogenic Fe fraction is important due to its high water solubility by the presence of Fe(III) sulfate.

(ii) Marine aerosol samples originated from volcanic ash were collected in the western North Pacific during KH-08-2 cruise (August, 2008). XAFS suggested that Fe species of volcanic ashes changed during the long-range transport, while dissolution experiment showed that Fe solubility of the marine aerosol is larger than that of volcanic ashes, possibly due to the transform of insoluble Fe in volcanic ashes into highly soluble Fe such as Fe(II) sulfate. It was found that the soluble Fe content in the aerosol supplied as volcanic ashes should be important due to its very high content of soluble Fe.

(iii) A series of recent studies showed that Fe in anthropogenic aerosols is more soluble than that in natural aerosols (Takahashi et al., 2013) and has lower isotopic ratio (Mead et al., 2013). However, the difference between Fe isotopic ratio ( $\delta^{56}\text{Fe}$ :  $[(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}}] - 1$ ) of two origins reported in Mead et al. (2013) is not so large compared with the standard deviation. Therefore, the aim of this study is to determine Fe species and  $\delta^{56}\text{Fe}$  in anthropogenic aerosols more accurately and to evaluate its contribution to the ocean surface.

Dominant Fe species in the samples were, ferrihydrite, hematite, and biotite. It was also revealed that coarse particles contained more biotite and that fine particles contained a larger amount of hematite, which suggested that anthropogenic aerosols were emitted during combustion processes. In addition, results of Fe isotopic ratio analysis suggested that  $\delta^{56}\text{Fe}$  of coarse particles were around +0.25‰, whereas that of fine particles were from -0.5 to -2‰, which was lower than the  $\delta^{56}\text{Fe}$  in anthropogenic aerosol by Mead et al. (2013). The size-fractionated sampling made it possible to determine the  $\delta^{56}\text{Fe}$  in anthropogenic aerosol. Soluble component in fine particles extracted by simulated rain water also showed much lower  $\delta^{56}\text{Fe}$  ( $\delta^{56}\text{Fe} = -3.9\text{‰}$ ), suggesting that anthropogenic Fe has much lower isotopic ratio. The remarkably low  $\delta^{56}\text{Fe}$  may be caused by the anthropogenic combustion process. The  $\delta^{56}\text{Fe}$  in anthropogenic aerosol measured here is important to model the budget of iron in the surface ocean.

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