

Low Iron Isotope Ratio in Aerosol Emitted by Combustion: Verification of Isotope Fractionation during Evaporation

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Primary biological production in the ocean is limited by the Fe deficiency (Martin and Fitzwater, 1988). Anthropogenic iron (Fe) in the atmosphere emitted by combustion can be one of the most important sources of dissolved Fe in the surface ocean because anthropogenic Fe is more soluble to water compared with natural Fe (Sedwick et al., 2009; Takahashi et al., 2013). It has also been reported that anthropogenic Fe is usually black and can affect the climate due to its positive radiative forcing (Moteki et al., 2017). Therefore, it is important to understand source, solubility, species, and environmental behavior of anthropogenic Fe.

Stable isotope ratio can reflect reaction process and/or sources, which makes it an efficient tool in environmental geochemistry. However, there has not been many studies about Fe stable isotope ratio ($\delta^{56}\text{Fe}(\text{‰}) = (^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-014}} - 1$) of anthropogenic Fe in aerosols (Flament et al., 2008; Mead et al., 2013). Our previous study revealed that $\delta^{56}\text{Fe}$ values of anthropogenic Fe were 4‰ lower than those of crustal Fe (Kurisu et al., 2016). We considered that the isotope fractionation is caused by the kinetic isotope fractionation during combustion. Therefore, this study aimed to understand Fe isotope fractionation processes during formation of anthropogenic Fe. Iron species was also investigated to know detailed formation process of anthropogenic Fe.

To get such samples with source information, we collected 7 size-fractionated aerosols near a steel plant. Iron stable isotope ratio and chemical species were analysed by multicollector ICP-MS and X-ray absorption fine structure (XAFS) spectroscopy, respectively. Scanning/transmission electron microscope (SEM /TEM) was also used for the speciation and morphology analyses.

Atmospheric Fe concentrations were high when wind came mainly from the direction of the steel plant. During these periods, enrichment factors ($\text{EF}: [\text{Fe}/\text{Al}]_{\text{aerosol}} / [\text{Fe}/\text{Al}]_{\text{crust}}$) were also high, suggesting that influence of emission from the steel plant was large.

Iron speciation for bulk samples showed that Fe(II)O was contained in coarse particles. By individual analyses, it was also found that such particles had similar component with slag, indicating that the coarse particles contained primary particles emitted during Fe manufacturing process. In the fine particles, on the other hand, Fe(II)O was not found but magnetite and ferrihydrite were mainly observed. It was also found that most of Fe-rich particles were spherical. These results suggested that they were formed under high temperature combustion process.

Iron isotope ratios of the coarse particles ($\delta^{56}\text{Fe} = -0.15 \sim +0.05\text{‰}$) were similar to those of Fe ore ($\delta^{56}\text{Fe} = -1 \sim +1\text{‰}$; Johnson et al., 2008) and terrestrial crust (0.00‰; Beard et al., 2003). On the other hand, the fine particles (0.39-0.69 μm) showed much lower Fe isotope ratio ($\delta^{56}\text{Fe} = -1.43 \sim -4.07\text{‰}$) than the coarse particles. It was suggested that Fe isotope in the fine particles was fractionated during combustion. This process can be explained by the Rayleigh's evaporation model. It is considered that the fractionation is decided by many factors including combustion temperature and chemical species.

Keywords: Iron isotope ratio, Anthropogenic Fe in aerosol, Isotope fractionation