

Speciation and isotope ratios of Fe in biomass burning aerosols and anthropogenic aerosols

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1. Introduction

Iron (Fe) in combustion aerosols emitted mainly by human activities exerts various effects on the environment and human health. The deficiency of dissolved Fe limits phytoplankton growth in some areas in the open ocean. Since supply of Fe to the surface ocean stimulates primary production and affects carbon and nitrogen cycles, many studies have been conducted regarding Fe cycle in the ocean. The main sources of Fe to the surface ocean are natural aerosols (mainly aeolian dust), dissolution of coastal sediment, and hydrothermal vents, whereas Fe in combustion aerosols has been recognized as another possible Fe source due to its high solubility to seawater. In addition, biomass burning is an important source of soluble Fe transported to the open ocean. Iron isotope ratios can be used as a tracer because Fe emitted by combustion can yield low Fe isotope ratios due to isotope fractionation during evaporation processes. However, data on Fe isotope ratios of various aerosol particles such as naturally-occurring aerosols, volcanic ash, biomass burning aerosols and anthropogenic aerosols emitted during combustion processes are lacking. Moreover, speciation of Fe in aerosols is also linked to the isotopic fractionation, since Fe emitted by the combustion processes mainly take Fe oxides and Fe hydroxide forms. Thus, combination of speciation of Fe in aerosols and determination of Fe isotope ratio is important to identify and quantify the Fe in aerosols supplied by various natural and anthropogenic processes.

2. Fe in aerosols emitted by biomass burning

Biomass burning is an important source of soluble Fe transported to the open ocean; however, its exact contribution remains unclear. Iron isotope ratios ($\delta^{56}\text{Fe}$) can be used as a tracer because Fe emitted by combustion can yield low Fe isotope ratios due to isotope fractionation during evaporation processes. However, data on Fe isotope ratios of aerosol particles emitted during biomass burning are lacking. We collected size-fractionated aerosol samples before, during, and after a biomass burning event and compared their Fe isotope ratios. On the basis of the concentrations of several elements and Fe species determined by X-ray absorption fine structure (XAFS) spectroscopy and micro-XAFS conducted at BL-12C and BL-4A, respectively, we found that Fe emitted during the

event mainly comprised suspended soil particles in all the size fractions. Iron isotope ratios of fine particles before and after the event were low due to the influence of other anthropogenic combustion sources, but they were closer to the crustal value during the event because of the influence of Fe from suspended soil. In this study, functional group analysis of carbon in each aerosol particle by scanning transmission X-ray microscopy (STXM) coupled by X-ray absorption near-edge structure (XANES) measured at BL-13A/BL-19A was also used to estimate temperature during formation of biomass burning processes.

3. Fe in aerosols emitted from Fe steel plant

On the other hand, Fe in anthropogenic aerosols emitted from a steel plant was also investigated in our study, and its formation process of anthropogenic Fe with low $\delta^{56}\text{Fe}$ was discussed. The samples contained a large amount of submicron spherical Fe oxide particles in fine size fraction, suggesting that the particles were emitted by high-temperature evaporation. Fine particles yielded much lower $\delta^{56}\text{Fe}$ values (as low as $-3.34 \pm 0.36\%$) than coarse particles (on average $0.09 \pm 0.19\%$), indicating that Fe isotope fractionation occurred during evaporation in the steel plant. The Fe speciation emitted from the plant was also examined by X-ray absorption fine structure (XAFS) spectroscopy and micro-XAFS conducted at BL-12C and BL-4A, respectively, it was found that Fe species were mainly wüstite (FeO), magnetite (Fe₃O₄), ferrihydrite, maghemite ($\beta\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$), but natural minerals of Fe-containing aluminosilicates (e.g., biotite and illite) were scarce, suggesting that Fe were mainly from the steel plant. Based on the isotope mixing plot and results of extraction experiment, the estimated $\delta^{56}\text{Fe}$ value for evaporated Fe was -4.1% . From mass balance calculation using -4.1% as the representative $\delta^{56}\text{Fe}$ value for evaporated Fe, its contribution was approximately $43\% \pm 8\%$ of the total soluble Fe in aerosols in a part of the Northwest Pacific, implying the large contribution of anthropogenic Fe.

References

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