Very low isotope ratio of iron in anthropogenic aerosols related to its contribution to the surface ocean: A speciation and isotopic study

Iron (Fe) is an essential nutrient for phytoplankton, but its concentration in surface seawater is very low, since Fe(III) is normally insoluble in seawater (approximately pH 8). Thus, phytoplankton growth in high-nutrient, low-chlorophyll (HNLC) regions is limited by the soluble Fe concentration [1]. The sources and budget of soluble Fe on the surface ocean should be clarified because phytoplankton plays an important role in the carbon cycle through photosynthesis, which can eventually affect climate change [2]. It has been suggested that aerosols deposited from the atmosphere may be the main source of Fe in HNCL regions in open oceans. However, the source of the aerosols that controls the amount of soluble Fe remains debatable. In modern systems, aerosols are generally classified into two origins, namely anthropogenic and natural [3]. The different formation processes cause varying solubility ranges of Fe in aerosols. The seawater-soluble fraction of anthropogenic Fe species is higher than that of Fe-containing dust, and anthropogenic aerosols can serve as soluble Fe sources on the surface ocean. However, the relative contribution of Fe in anthropogenic aerosols to the soluble Fe fraction in seawater in actual systems remains unclear. One of the tools to determine the contribution of Fe from different sources is the Fe stable isotope ratio, which is generally used to discuss the geochemical cycles of various elements on the Earth's surface. If the Fe stable isotope differs between anthropogenic and dust aerosols, the contribution of anthropogenic Fe in aerosols to the surface ocean can be estimated. In this study, the Fe isotope ratios of aerosols in seven size-fractionated samples were measured to identify the Fe isotope ratio of the anthropogenic component. The soluble fraction and chemical species of Fe in aerosols were determined through leaching experiments and X-ray absorption fine structure spectroscopy (XAFS), respectively. These results can be related to the source of Fe in aerosols and subsequent Fe-related chemical processes in the atmosphere during transport. The size dependence of the Fe stable isotope ratio and Fe species helped identify the anthropogenic Fe species and their isotope ratios, which are associated with the soluble fraction of Fe in the surface seawater.

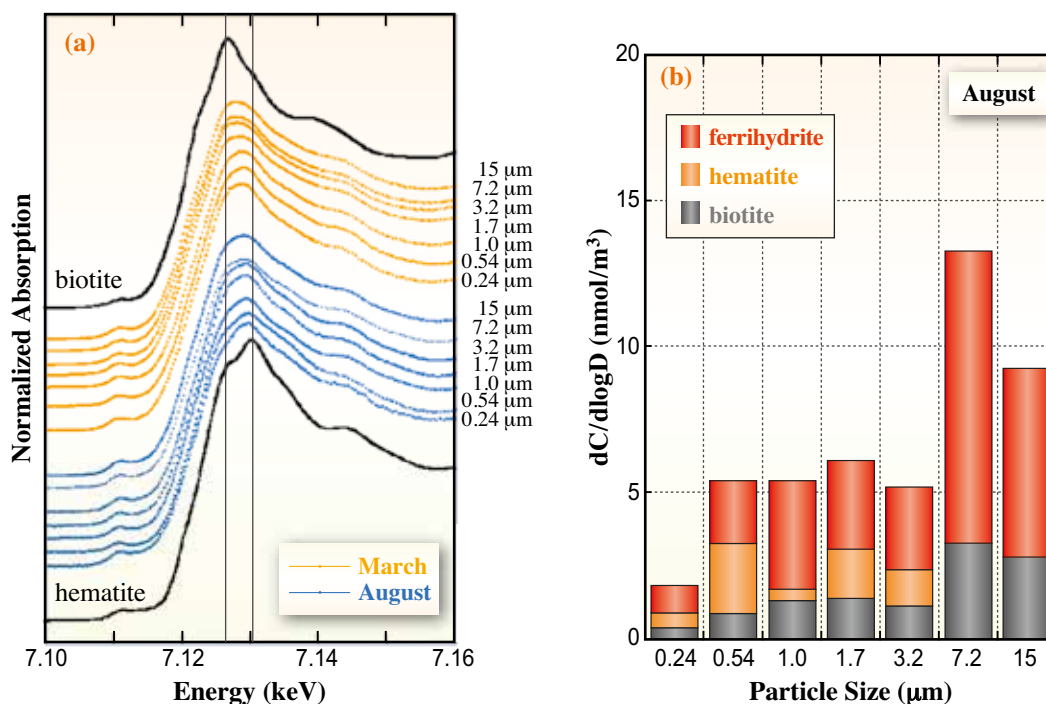With this background, we have measured Fe K-edge XAFS at SPring-8 **BL01B1** and **BL37XU** to determine

Fig. 1. (a) XANES spectra of aerosol samples with different particle sizes; (b) Iron concentration of each Fe species determined by XAFS analysis.

the average Fe species in bulk aerosol samples and the Fe speciation for single particles, respectively. The iron isotopes of Fe for different particle sizes were measured by a multi-collector ICPMS (Neptune) installed at the Department of Earth and Planetary Science, The University of Tokyo. The aerosol samples employed in this study were collected in March and August 2013 in an urban environment in Higashi-Hiroshima, Japan, and in a marine environment (northwestern Pacific).

The leaching experiments revealed that the iron in the fine particles in the urban sample was more soluble in simulated seawater (approximately 25%), compared with less than 10% for Fe in the coarse particles. XAFS analysis (Fig. 1) showed that the hematite fraction was larger in the fine particles than in the coarse particles, whereas biotite/chlorite (a natural mineral) was relatively more abundant in the coarse particles than in the fine particles as reported previously [4]. Although the ferrihydrite and hematite in the coarse particles of crustal origin, which may have undergone alteration during the long-range transport, dominate the Fe species for bulk aerosols [5], the main Fe species in the finer aerosols are most likely ferrihydrite and hematite produced by anthropogenic processes.

The μ-XANES results for some particles collected in Higashi-Hiroshima showed high intensities of Fe with (i) relatively strong signals of V and nickel (Ni) and (ii) a weaker signal of K. Particles could not be distinguished individually because of their finer size than that of the X-ray microbeam. However, the presence of V and/or Ni, which are often used as indicators of aerosols produced through fossil fuel combustion, suggests that the particles were emitted during combustion processes. Ferrihydrite and hematite were the main Fe chemical species of the particles, which again suggested that the oxidized species were emitted during the combustion processes.

The Fe isotope ratios ($\delta^{56/54}$Fe) of the coarse particles were close to the crustal value (0.04‰ to 0.30‰) (Fig. 2). By contrast, the Fe isotope ratios of the fine particles, ranging from −0.56‰ to −2.01‰, were lower than the crustal value. The $\delta^{56/54}$Fe values of the soluble fraction in the fine particles were very low (−1.87 to −3.91‰), suggesting that anthropogenic aerosols have a very low Fe isotope ratio. The very low Fe isotope ratio (δ^{56}Fe= −3.91‰) could be observed in this study because of the successful separation of anthropogenic components in aerosols collected in Higashi-Hiroshima. This value was the lowest among the reported $\delta^{56/54}$Fe values of materials collected on the Earth's surface environment because of the much larger isotopic fractionation through combustion. This

large isotope fractionation can be explained by the kinetic isotope fractionation during the combustion of Fe species at high temperatures coupled with the refractory characteristics of Fe.

Marine aerosols around the northwestern Pacific were also analyzed. The Fe isotope ratio in the fine particles was also lower than that in the coarse particles. This finding indicates that anthropogenic aerosols contribute to marine aerosols. These results may be important to quantitatively estimate anthropogenic Fe components deposited on the surface ocean on the basis of the Fe isotopes of possible Fe components supplied to the surface ocean.
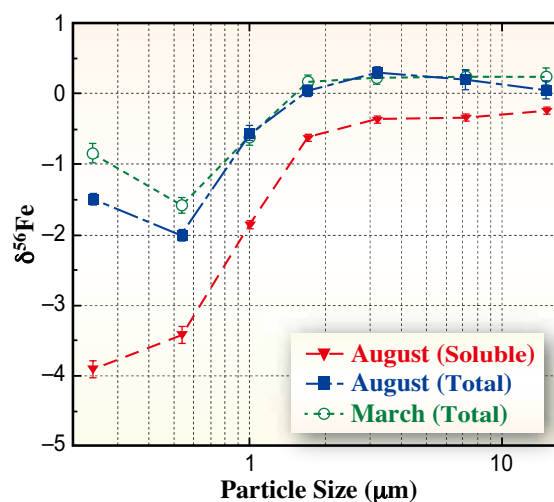

Fig. 2. Iron isotope ratios for aerosol samples given by $\delta^{56/54}$Fe(‰)={(^{56}Fe/^{54}Fe)$_{sample}$/(^{56}Fe/^{54}Fe)$_{IRMM-014}$ −1}×1000 for total Fe and water-soluble components.

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