

## Seasonal changes in Fe species and soluble Fe concentration in the atmosphere in the Northwest Pacific region based on results of the speciation analysis of aerosols collected in Japan

Oceanic areas where phytoplankton growth is limited by iron (Fe) concentration are called "high-nutrient, low-chlorophyll (HNLC)" regions [1], which account for 20% to 30% of the world's oceans [2]. The concentration of bioavailable Fe in the euphotic zone in the ocean can affect the photosynthesis of phytoplankton in HNLC regions, which can consequently affect the carbon cycle on the Earth's surface. Moreover, the amount of Fe in remote oceans can increase the production of dimethyl sulfide and/or organic carbon from microorganisms in the ocean, which in turn can affect the radiative forcing in the atmosphere [2]. Thus, understanding the processes of Fe supply and the dissolution of Fe from the atmosphere into the ocean is essential for estimating the impact of Fe on the Earth's climate.

The bioavailability of Fe in aerosols depends mainly on the fraction of soluble Fe ( $=[\text{Fe}_{\text{Sol}}]/[\text{Fe}_{\text{Total}}]$ , where  $[\text{Fe}_{\text{Sol}}]$  and  $[\text{Fe}_{\text{Total}}]$  are the atmospheric concentrations of soluble Fe and total Fe, respectively). However, numerous factors affecting the soluble Fe fraction have not been fully elucidated. In this study, the Fe species, chemical composition, and soluble Fe concentration in aerosols collected in Tsukuba, Japan over a year (nine samples from December 2002 to October 2003) were investigated to identify the factors affecting the amount of soluble Fe supplied into the ocean. The soluble Fe concentration in aerosols correlates with the concentrations of sulfate and oxalate originating from anthropogenic sources, suggesting that soluble Fe is mainly derived from anthropogenic sources. Moreover, the soluble Fe concentration correlates with the enrichment factors of vanadium and nickel emitted

by fossil fuel combustion. These results suggest that the degree of Fe dissolution is affected by the magnitude of anthropogenic activity, such as fossil fuel combustion.

Hence, X-ray absorption fine structure (XAFS) spectroscopy was performed in this study at beamline **BL01XU** to identify the Fe species in aerosols [3]. The speciation of various elements in aerosols has been successfully conducted for calcium, zinc, and iron [4,5]. In Figs. 1 and 2, examples of X-ray absorption near-edge spectroscopy (XANES) profiles and extended X-ray absorption fine structure (EXAFS) spectra are respectively shown with the fitting results obtained by a linear combination of the spectra of possible Fe species. The fitting of XANES profiles and EXAFS spectra coupled with the results of micro-X-ray fluorescence analysis ( $\mu$ -XRF; data not shown) revealed the main Fe species in the aerosols collected in Tsukuba to be illite, ferrihydrite, hornblende, and Fe(III) sulfate (Fig. 3). In particular, the illite fraction increases in spring, possibly due to the illite contributed by the arid area in East China, which can be transported to Japan via dust events that often occur in spring (Fig. 3).

On the other hand, the Fe(III) sulfate fraction reached about 15-20% of the total Fe from May to August (Fig. 3). On the basis of the results of backward trajectory analyses, the air mass in Tsukuba during that period came from the south part, or from industrial areas in Tokyo, which was supported by the increase in Zn and Cu concentrations during the period. Moreover, the soluble Fe fraction in each sample measured by leaching experiment was also

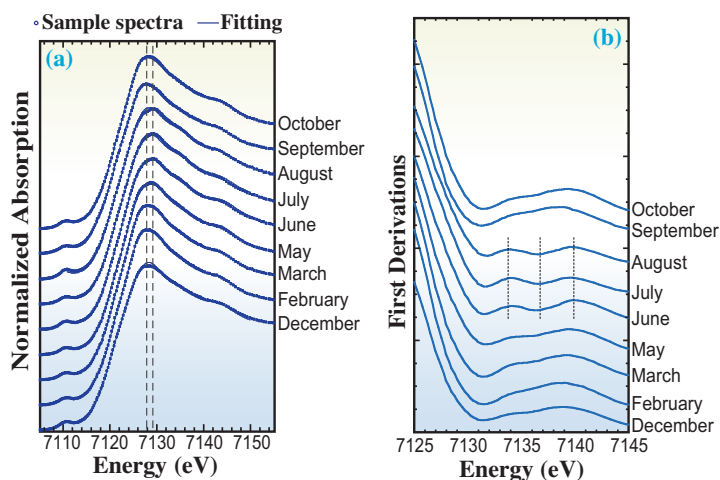


Fig. 1. (a) Fitting of Fe K-edge XANES spectra of aerosols collected in various months and (b) their first-derivative spectra.

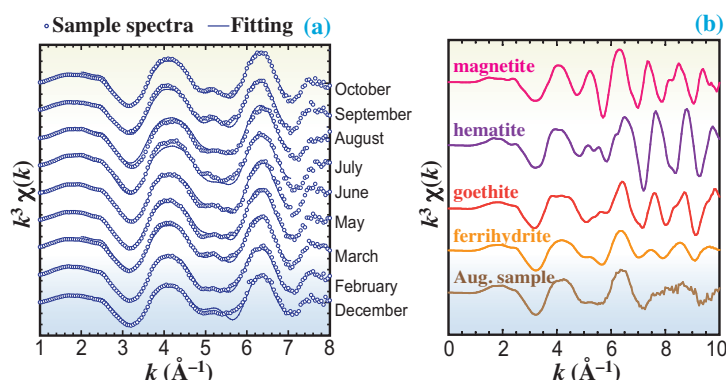


Fig. 2. (a) Fitting of Fe K-edge EXAFS spectra in k space of aerosols collected in various months with (b) the reference spectra for various Fe oxide species.

high during the period, which closely correlated with the Fe(III) sulfate fraction determined by the XAFS spectrum fitting, suggesting that Fe(III) sulfate is the main soluble Fe species from aerosols that is dispersed into the ocean.

Another possible factor that can control the amount of soluble Fe dispersed into the ocean is the total Fe(III) concentration in the atmosphere, which was high in spring owing to the high mineral dust concentrations during the period (= i.e., March in Fig. 4(a-1)). However, this factor does not contribute to the amount of soluble Fe to a larger degree than the effect of Fe speciation. The contribution of each species to the total amount of Fe during the whole year was largest for ferrihydrite, whereas the contribution to soluble Fe was largest for Fe(III) sulfate (Fig. 4(b)). As a result, the amount of soluble Fe is larger in May, June, and July owing to the presence of Fe(III) sulfate during this period (Fig. 4(a-2)).

On the basis of the above results, it was concluded that the most significant factor influencing the amount

of soluble Fe in the North Pacific region is the concentration of anthropogenic Fe species, such as Fe(III) sulfate, that emitted from megacities in East Asia.

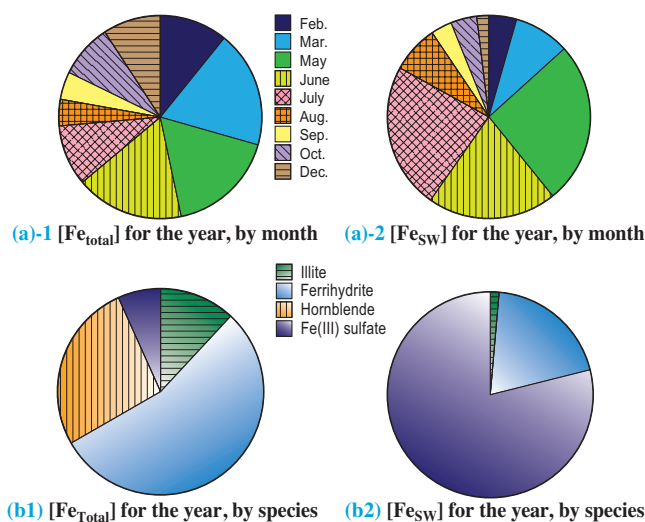


Fig. 4. (a) Contribution of each month to (a-1) total [Fe<sub>Total</sub>] and (a-2) total [Fe<sub>SW</sub>] for the year and (b) contribution of each species for (b-1) total [Fe<sub>Total</sub>] and (b-2) total [Fe<sub>SW</sub>] in the year. Note that the sampling was conducted only in February, March, May, June, July, August, September, October, and December.

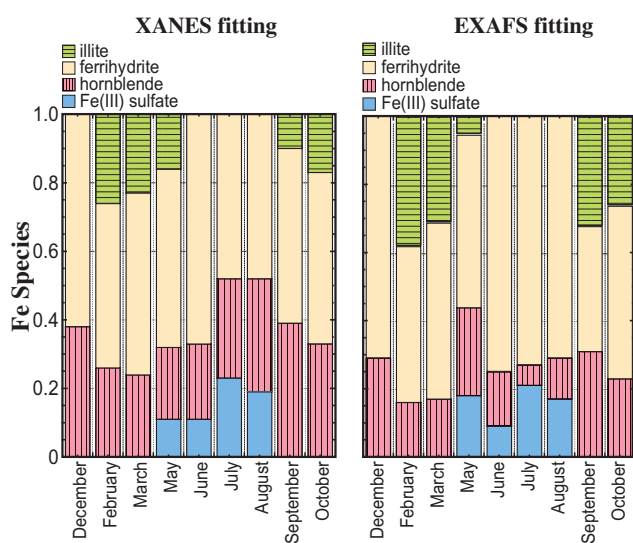


Fig. 3. Iron species in aerosols estimated by (a) XANES fitting and (b) EXAFS fitting.

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