

Characterization of iron in airborne particulate matter by XANES technique

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Introduction

Elucidating the chemical property and dynamic change process of airborne particulate matter is important. Metal complex in airborne particulate matter needs to be investigated in order to assess the chemical reaction on its surface. Iron is one of the most abundant elements in airborne particulate matter. Iron compounds are introduced from various natural and, at the same time, anthropogenic sources into the atmosphere. The chemical species of iron in airborne particulate matter are reported very widely according to origin, such as soil and exhaust of combustion engines, by ⁵⁷Fe Mössbauer spectroscopy. Therefore, for identifying the origins of aerosol, the chemical states of iron in airborne particles merits investigation. In this report, we have applied XANES to characterize the chemical states of iron in particulate matter samples. In addition, an attempt was made to quantify the chemical species of iron in airborne particles by applying partial least-squares (PLS) method [1].

Experimental

The sampling was carried out at the campus of The University of Tokyo in early October 2000. This sampling site is located in urban area in Tokyo, Japan. Airborne particles were collected by four-staged Andersen air sampler equipped with a back-up filter. The standard reagents, the mimetic chemical compounds for supposed form of iron compounds in airborne particles, were measured to compare with the airborne particle samples. The standard chemical reagents, whose chemical species are olivine ((Fe,Mg)₂SiO₄), iron (III) sulfate (Fe₂(SO₄)₃) and iron (III) oxide (Fe₂O₃) were also used for PLS modeling.

The XAFS measurement was performed using synchrotron radiation ring at BL-12C, Photon Factory, KEK, Japan [2]. A Si (111) double-crystal monochromator was used. The iron K-edge XANES spectra of the samples were measured in a fluorescence mode using a Lytle-type detector.

Results and Discussion

The XANES spectra of olivine, iron (III) sulfate and iron (III) oxide which were selected as model compounds seem to cover almost the whole range, where the spectra of airborne particles lie. The absorption edge of fine particle shifted towards higher energy than that of coarse particle. The oxidation state of iron species increases with

decreasing grain sizes, and increasing with contribution of anthropogenic effects. From this fact, it is suggested that the edge energy of spectrum is regarded as an index of anthropogenic effects. Figure 1 shows relative abundance of iron species estimated from the PLS calculation. Relative abundance of Fe (II) component decreases with a decrease in grain size. Most Fe (II) is found in nature as silicates and the size of the particles in which Fe (II) is found is usually larger compared with grain sizes where Fe (III) is dominated.

In this work, we were able to estimate the relative abundance of chemical species of iron by applying PLS modeling to XANES data. This paper can be possible path way to wider application of XANES and PLS modeling to chemical speciation of metals in airborne particle samples.

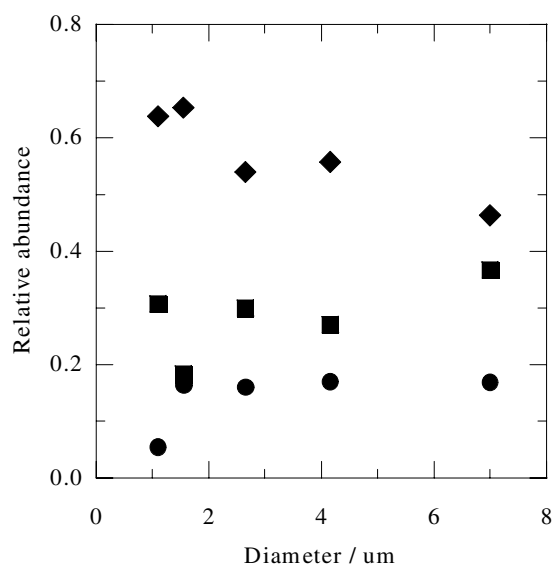


Figure 1. Relative abundance of iron species in airborne particles as determined by PLS modeling: ●, ferrous silicates (olivine); ■, ferric sulfate (Fe₂(SO₄)₃); and ◆, iron oxide (Fe₂O₃).

References

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