Selected Article

Analysis of Atmospheric Particulate Matter in Antarctica

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The author, who is a staff member of Horiba, Ltd., stayed for one year at Showa Station, Antarctica as a member of the 49th Japanese Antarctic Research Expedition (JARE49th) and observed atmospheric particulate matter with an XGT-5000WR X-ray analytical microscope. This was the first time that particulate matter had been analyzed at Showa Station using an X-ray analytical microscope, and this paper is a preliminary report of the analysis.

Introduction

The observation of particulate matter at Showa Station was done through number concentration measurement using an optical particle counter,[1] condensation particle counter and micro pulse lidar.[2] On the other hand, the particulate matter elements were analyzed by physical and chemical analysis after the samples had been brought back to Japan.

The samples were subject to the problem of alteration. JARE has had only one chance per year to ship cargo from Showa station, and in some cases more than one year passed between the gathering and the measurement of samples, therefore it was difficult to remove the influence of alteration. There were no analytical tools to measure the samples in Showa Station. As a result, it was difficult to create the optimum conditions for sampling. To solve this problem, particulate matter in the Antarctica region was analyzed by X-ray fluorescence microscope in Showa station with no alterations.

Particulate Matter

For particulate matter, the diameter is between 10 nm and 100 μm and the origin differs according to the element as shown in Figure 1. The particulate matter has become cloud nuclei, influencing cloud formation. There is also an influence on the global environment due to interception of solar radiation and contaminant adsorption.

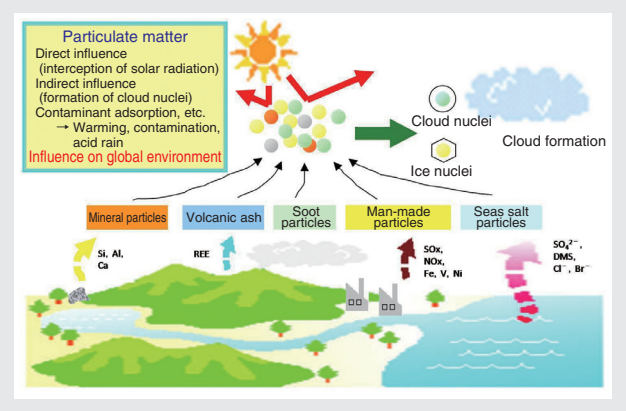

Figure 1 Origin of particulate matter
REE: Rare Earth Element
DMS: Dimethly Sulfide

X-Ray Fluorescence Microscope

The XGT-5000WR X-ray Fluorescence microscope can obtain an optical image, transmitted x-ray image, and X-ray fluorescence (XRF) mapping image of the sample by arranging optics CCD, transmitted X-ray detectors, and the irradiation X-ray system on the same axis, and scanning the sample stage in the direction of XY.

Figure 2 shows the device concept chart. In the bulk analysis of gathered particulate matter, XRF can do quantitative and qualitative analysis without destroying the sample though it is difficult to analyze the particles individually because the irradiation diameter of X-ray guide tube[3] used is 100 μm or 1.2 mm in this observation.

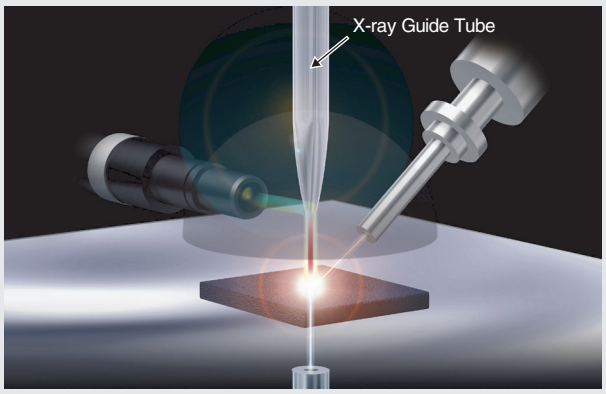

Figure 2 Device concept chart

This is very useful as the screening analysis before ICP etc. are precisely analyzed.

Analysis of Particulate Matter

The sampling conditions were as follows.
- Sampling flowrate : 7 l/h
- Sampling time : 24 h
- Sampling filter : PTFEfilter

XRF mapping condition

- X-ray tube voltage and current : 50 kV • 1 mA
- X-ray target : Rh
- Mapping area : 7.154×7.154 mm^2
- Number of pixels : 256×256 pixels
- Mapping elements : Na, Mg, Al, Si, S, Cl, K, Ca, Fe, Zn, Br
- X-ray irradiation diameter : 100 µmø

XRF analytical condition

- X-ray tube voltage and current : 50 kV • 1 mA
- X-ray irradiation diameter : 1.2 mmø

Particulate matter was sampled in the clean atmospheric observation room of Showa station. There was a possibility that the density of a particulate matter was insufficient in sampling by a low volume sampler because the number concentration of particulate matter in the Antarctica region was very low compared with a civilized region.
Therefore, the sampling diameter of particulate matter, which was 10 mmØ up to that point, was adjusted to 3 mmØ and the collection density of particulate material was improved. The analysis of the sample performed XRF mapping first, and extracted the part to which the particulate matter thoroughly adheres in the collected particles. The bulk was analyzed by the X-ray irradiation diameter of 1.2 mm for the part. Figure 3 and 4 each show the XRF spectrum of the collected part and the XRF mapping image of the collected particulate matter.

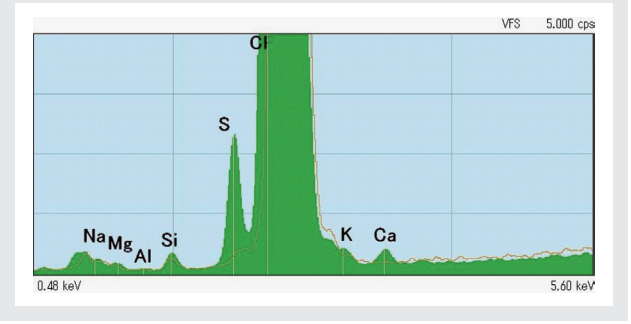

Figure 3 XRF spectrum of particulate matter

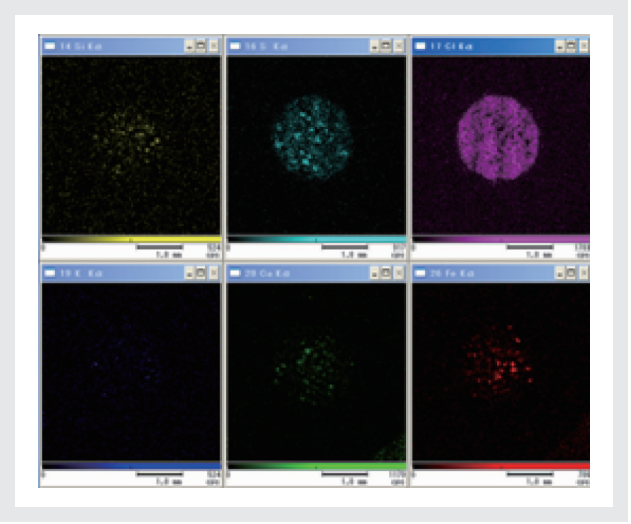

Figure 4 XRF mapping image of particulate matter collected on the filter

Annual Fluctuation of each Element of Particulate Matter

Figure 5 and 6 are plotted analysis results of particulate matter over time. The particulate matter elements in Showa station are divided into SOx (CH_3SO_3-,nss-SO_4-), nitrogen oxide (NO_3-), sea salt particles, and soil particles, among others.
The most distinctive feature of this observation was sulfur thought to be of SOx origin that showed a trend to increase in summer, and to decrease in winter. Because dimethyl sulphide (DMS) and DMSO that the marine plankton chiefly discharges are resolved and react to solar radiation,[4], [5] particulate matter of sulfur is generated. It is thought that DMS etc. discharged from the marine plankton and the penguin colony increased due to the influence of solar radiation in summer when the living organisms become active, and thus the number of particulate materials of SOx increased.
Sea salt particles (Na, Mg, Cl, Ca) increased at the time of strong winds such as blizzards. These sea salt particles, chiefly generated from the open water surface of the Southern Ocean, are transported by the disturbance of

low-pressure. Moreover, it is considered that air-bound snow which originates in the denudation in the snowfall layer where the salinity concentration is high contributes to an increase in sea salt particles at the time of blizzard.[6] The amount of sea salt particles decreased in summer, and sea salt particles were not detected by XRF analysis. This was due to a decrease in blizzards and snow accumulation.

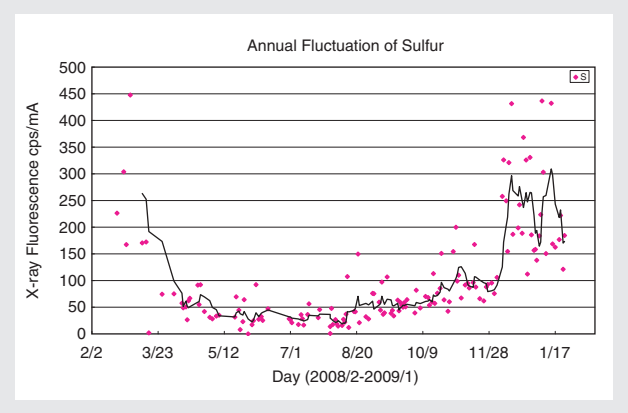

Figure 5 Annual fluctuation of sulfur

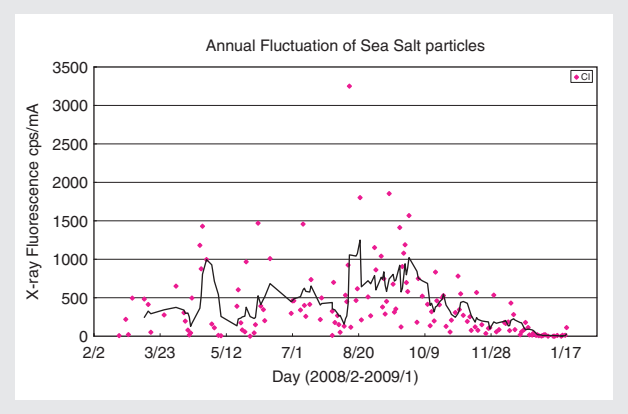

Figure 6 Annual fluctuation of sea salt particles

Conclusion

JARE is continuing to conduct observation in this harsh environment. Any breakdown of the observational equipment is fatal due to the cargo shipment being only once a year. Nevertheless, the X-ray analytical microscope that we had brought to Showa Station was able to complete the one-year observation safely. This result shows that it is possible to bring more sensitive analytical instruments in the future.

References

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