

Observation of transformation of calcite to gypsum in mineral aerosols by Ca K-edge X-ray absorption near-edge structure (XANES)

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A large amount of sulfate aerosols is produced in East Asia because of the large emission of SO₂ mainly caused by coal burning in China. Among the various environmental influences related to SO₂ emission, the acidification of soil and natural water by wet and dry depositions originating from SO₂ has been widely discussed, similarly with NO_x species. The acidity of gaseous and aerosol SO_x species (including SO₂, sulfuric acid, and other acidic sulfate salts in this report) can be mitigated by their neutralization through alkaline salts such as calcium carbonate in mineral aerosols, where the transformation of Ca species from calcium carbonate to calcium sulfate has been suggested. From this viewpoint, large amounts of mineral aerosols produced in northwestern China and Mongolia contribute to the decrease of the acidity caused by acidic SO_x species. Although the neutralization effect by mineral aerosols was indicated in various studies, it is often the case that the information on the chemical species in such studies have been estimated through indirect methods such as elemental analyses by proton-induced X-ray emission spectroscopy, electron microscopy with energy-dispersive X-ray spectrometer, chemical analysis of water-soluble elements, etc. In order to obtain a clearer description of the neutralization effect, identification of the chemical species of Ca in aerosols is indispensable in knowing the ratio of calcium carbonate and gypsum related to the degree of neutralization.

In the present study, Ca K-edge XANES measured at BL-9A at Photon Factory was employed for the speciation of Ca in mineral aerosols collected by an Andersen-type air sampler in Aksu, close to the Taklimakan Desert in China. The sampling was conducted in April 2002 when dust events occurred. Additionally, the sample collected in January 2002 was studied for comparison purposes as well. It was found that the XANES spectra of mineral aerosols can be well simulated by those of calcite and gypsum, which can provide the ratio of gypsum to calcite (or total Ca minerals) in the samples. Moreover, we measured the XANES in both the fluorescence (FL) and conversion electron/He-ion yield (CEY) modes, which are bulk and surface-sensitive analysis, respectively. Based on the XANES data, several conclusions were deduced in this study (Fig. 1): (1) The similarity of spectra recorded in the two modes in April suggest that the gypsum fraction

(~ 10%) in the period reflects the ratio of gypsum to the total Ca minerals in the source area without a significant effect of the formation of the secondary gypsum produced at the surface of the mineral aerosols; (2) A larger gypsum fraction detected in the CEY mode than in the FL mode in January reveals that gypsum is mainly found at the particle surfaces, suggesting that the gypsum in this period was mainly produced secondarily by the reaction of calcite with the acidic SO_x species during the transport; (3) Considering the neutralization of acidic SO_x species by calcite in mineral aerosols, the Ca speciation data obtained here may be explained by (i) the large supply of mineral aerosols including calcite in April as well as (ii) the large anthropogenic emission of SO₂ generally found in winter in China (which is in January).

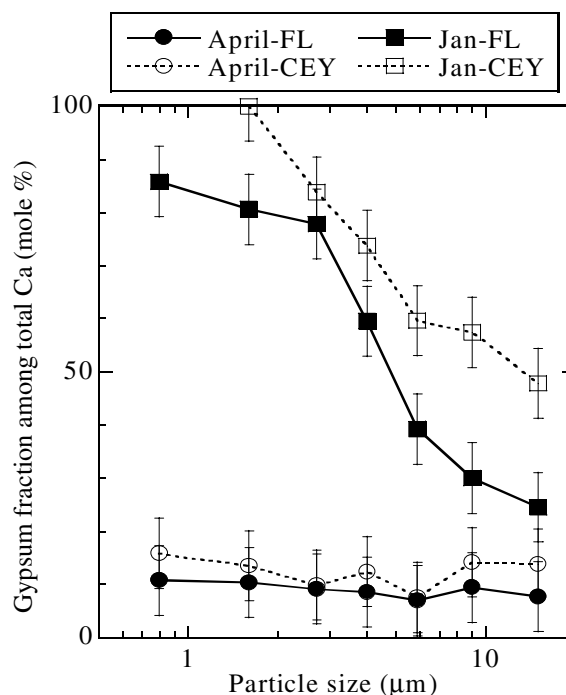


Fig. 1. Gypsum fraction among total Ca minerals determined by FL- and CEY-XANES for the samples collected in January and April.

References

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