Neutralization of Acidic Sulfur Species by Calcite in Mineral Aerosols Collected in China and Japan Studied by Ca K-Edge X-Ray Absorption Near-Edge Structure Spectroscopy

X-ray absorption near-edge structure studies at the calcium K-edge have been used to show that acidic sulfur species in the atmosphere (e.g., H₂SO₄) mainly released by human activities, can be neutralized by the calcite present in mineral aerosols produced in the arid areas of western China. In the neutralization process, gypsum is secondarily formed from the calcite in the aerosols. These processes are suggested since the gypsum fraction of the total Ca content increases with increasing transportation distance of the "Kosa" aerosol particles. In addition, use of the surface sensitive conversion electron yield method showed that gypsum is preferentially present at the surface of the particles.

A large amount of sulfate aerosol is produced in eastern Asia as a result of large emissions of SO₂, mainly from coal burning in China. The sulphate aerosols contribute to various effects, including global warming and respiratory health problems. Acidification can be mitigated by the neutralization of the acidic SO₄ species (SO₄⁺, sulfuric acid, and acidic sulfate salts in this study) by alkaline salts such as calcium carbonate, present in the mineral aerosols produced by dust events in Mongolia and West China. Although various studies have indicated this neutralization effect, results have been derived mainly from indirect chemical analyses of the aerosol samples, from which it is not easy to unambiguously determine the chemical processes occurring. It is necessary, therefore, to obtain a clearer understanding of the neutralization effect by the speciation of Ca in mineral aerosols.

In this study, Ca content in mineral aerosols collected simultaneously in Aksu, Qingdao, and Tsukuba during dusty and non-dusty periods was determined using Ca K-edge X-ray absorption near-edge structure (XANES). Size-fractionated aerosol samples were collected in March (dusty period) and January (non-dusty period) 2002 using a low-volume Andersen-type air sampler. The sampler had eight stages and a back-up filter. The particle diameters classified by aerodynamic diameter are as follows: >11.0 μm (sampling stage 0), 7.0–11.0 μm (stage 1), 4.7–7.0 μm (stage 2), 3.3–4.7 μm (stage 3), 2.1–3.3 μm (stage 4), 1.1–2.1 μm (stage 5), 0.65–1.1 μm (stage 6), 0.43–0.65 μm (stage 7), and < 0.43 μm (back-up filter).

From fits to the XANES spectra (Fig. 1), it was found that (i) calcite and gypsum were the main Ca species in the aerosol samples, and (ii) the gypsum fraction of total Ca mineral content [Gyp]/[Ca]⁺ increased progressively in the order Aksu < Qingdao < Tsukuba (Fig. 2), which is consistent with the direction of long-range transportation of mineral aerosols initially formed in the arid areas of western China during the large dust event in March, 2002. The results show that calcite originally present in the mineral aerosol was transformed into gypsum as a consequence of neutralization of the acidic sulfur species by calcite.

Surface-sensitive XANES spectra in the conversion electron yield mode (CEY) were also recorded. These showed that gypsum is formed selectively at the surface of the mineral aerosols for all samples, except for those collected in Aksu during the dusty period (Fig. 2). The decrease of the [Gyp]/[Ca]⁺ ratio with increasing particle size shows that the neutralization effect proceeds from the particle surface. For the Aksu sample in the dusty period, however, (i) the [Gyp]/[Ca]⁺ ratios obtained from the bulk-sensitive fluorescence-mode (FL) XANES spectra were similar to those obtained using the CEY mode, and (ii) no size dependence was found, showing that the neutralization effect is not important for this sample because of the large supply of mineral aerosol with little neutralization effect in Aksu. It was also found that the pH of the aerosol and the ratio of (NH₄)₂SO₄ to gypsum were positively and negatively correlated with the Ca (or calcite) content, respectively. Samples containing less calcite show lower pH values due to the exhausting of calcite by the neutralization effect. Although the mineral aerosols, known as “Kosa” in Japan, affect human health, lead to reduced crop harvests due to adhesion, and have a global radiative forcing effect, they can also have beneficial effects, such as the neutralization of acid precipitation, as indicated in this study.

As shown here, the speciation of Ca using XANES is important for revealing the neutralization processes of acidic sulfur species by calcite during the long-range transport of mineral aerosols from western China to Japan.

REFERENCES


Figure 1
Normalized Ca K-edge XANES spectra of Ca reference materials (gypsum, calcite, Ca(NO₃)₂, and anorthite) and aerosol samples collected in Qingdao (Jan-1, Jan-4, March-1, and March-4). “Jan-1” denotes the stage-1 sample collected in January, and the same notation is used for the other samples. An example fit to a linear combination of calcite and gypsum contributions (dotted line) is also shown for the March-1 sample.

Figure 2
Gypsum fraction of total calcium content [Gyp]/[Ca]⁺ for various particle sizes collected in Aksu, Qingdao, and Tsukuba during the dusty (March 2002) and non-dusty (January 2002) periods. Results obtained in both the FL (bulk sensitive) and CEY (surface sensitive) modes are shown.