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Depth-dependent Calcium Speciation in Individual Aerosol Particles by Combination of Fluorescence Yield and Conversion Electron Yield XAFS Using X-ray Microbeam

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Particle surfaces of mineral aerosols are important reaction sites in the atmosphere. Previous studies suggested that calcite in aerosols, which are emitted during dust periods, neutralizes sulfuric acid. In this study, depth-dependent X-ray absorption fine structure spectroscopy for individual particles was employed to determine calcium (Ca) species at particle surface and in the bulk of individual particles, using an X-ray microbeam measured in the conversion electron yield and fluorescence yield modes, which is a powerful method to understand chemical processes at aerosol surfaces.

Various chemical processes proceed at aerosol surfaces in the atmosphere. In particular, chemical reactions related to various important environmental phenomena can occur on particle surfaces.[1–3] Among them, calcite ($CaCO_3$) is a major reactive mineral in aerosols,[4] and is particularly abundant during dust events like Kosa in the eastern Asia, which is caused by mineral aerosols transported from arid area or desert in western China mainly in springtime.[5,6] On the other hand, sulfur dioxide (SO_2) is a reactive gaseous species produced mainly by coal burning and is emitted in urban areas in East Asia. SO_2 is oxidized in the atmosphere and converted to sulfuric acid (H_2SO_4), which finally forms sulfate aerosols.[7] These species have a large impact on the environment because of their acidities. However, it is reported that mineral aerosols like $CaCO_3$ can mitigate the acidities of SO_x species.[8]

Takahashi et al. observed the neutralization between $CaCO_3$ and H_2SO_4 in dust during its long-range transport from a desert area in western China to Japan.[9] They analyzed samples collected in Aksu (near the Taklimakan Desert), Qingdao (urban area in eastern China), and Tsukuba (eastern Japan) during a large dust event in March, 2002, using sulfur (S) and Ca speciation by S and Ca K-edge X-ray absorption near-edge structure (XANES) spectroscopy, or the structure near absorption edge in X-ray absorption fine structure (XAFS).[10] The main Ca species determined by the spectra were calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) and the mole ratio of gypsum to total Ca (= measured by ion chromatography) were estimated. The gypsum fraction, which is a neutralization product, relative to total Ca for the bulk analysis increased in the order from Aksu, Qingdao to Tsukuba. In that study, Ca K-edge XANES measured by both fluorescence yield (FY) and conversion electron yield (CEY) modes were simultaneously employed to aerosol samples collected on aerosol filters, which provide information on Ca species in the whole and at the surface of the particles, respectively. Coupling of the two modes enables us to compare gypsum fraction in the whole and at the surface of the particles. These results suggested that gypsum was formed at the surface of $CaCO_3$ particles by neutralization of H_2SO_4 in the atmosphere during long-range transport.

However, this analysis using mm-size X-ray beam still has a problem, because the method shows average Ca species as bulk analysis of lots of particles recovered on the aerosol filters. Thus, it is actually not clear whether the Ca at the surface of calcite is really transformed into gypsum in terms of individual particle analysis. This means that relatively larger ratio of gypsum at particles surfaces suggested by CEY mode does not indicate formation of gypsum at calcite surface, but the secondary formation of gypsum can occur at surface of other particles. In this study, X-ray fluorescence (XRF) mapping and Ca K-edge XANES measurement both in FY and CEY modes were conducted using a μm-size X-ray beam. This method, which can be referred to as depth-dependent μ-XAFS, allows Ca speciation of individual mineral aerosols both in the whole and at the surface of the particles, respectively.

Aerosol samples analyzed in this study were collected in Aksu and Qingdao during a large dust event (March, 2002). Particle size-fractionated samples were collected using a 9-stage Andersen-type air sampler (AN-200, Sibata, Tokyo). In this paper, we report analysis of aerosol samples with particle diameter 3.3–4.7 μm. Bulk Ca speciation of the same samples was already reported in Takahashi et al.[9] Details of the sampling locations etc. were given in Supporting Information.

Micro-XRF-XAFS analysis was conducted at beamline 10.3.2 at the Advanced Light Source in Lawrence Berkley National Laboratory, U.S.A.[11] Particles collected on the PTFE filter in the air sampler were dispersed on a carbon tape (JEOL, Tokyo, Japan). To identify Ca-rich particles, μ-XRF analysis was conducted for the aerosol particles on the carbon tape. Mapping was performed with a beam size of $5 \times 5 \, \mu m^2$ pixels, appropriate for identifying 3–5 μm particles collected in the sample. Subsequently, Ca K-edge μ-XANES spectra were measured for the Ca-rich particle using $6 \times 6 \, \mu m^2$ beam. The XRF and XANES spectra were measured in a cell with two electrodes purged with helium, which enables us to measure μ-XANES in CEY mode.[12] In addition, fluorescence X-ray was detected by a Canberra 7-element Ge detector (Ultra LEGe, 50 mm² per element) through a thin film of aluminized Mylar used as a window of the CEY cell. The probing depth of CEY-mode (= about 55 nm for Ca KLL emission defined as the depth where the escape probability of the electrons becomes $1/e$)[13] is much smaller than that of FY-mode. The analysis depth, rather than the probing depth, for FY-mode, which is free from the thickness effect that can attenuate peaks in XANES spectra,[14] can be practically larger than the aerosol particle size examined

here, because identical spectra between FY- and CEY-modes for unreacted calcite particles were obtained in the previous study (particle size 4.7–7.0 μm).[10] Hence, the combination of FY- and CEY-modes makes it possible to determine Ca species in the whole and at the surface of each particle.[9,10]

XANES spectra obtained were fitted by a linear combination of spectra of reference materials as reported in Takahashi et al.[10] to estimate mole ratios of Ca species present in individual particles. The least-squares fitting of the spectra was conducted using REX2000 (Rigaku Co., Tokyo, Japan).

The results obtained for the samples at Aksu are described first. Aksu is located in western China close to the Taklimakan Desert, which is the main source of dust transported there. It is expected that the degree of neutralization of calcite is much lower than that in eastern China, such as in Qingdao. Bulk FY- and CEY-XANES spectra using a millimeter-size beam for the Aksu sample[9] showed that the Ca species in the bulk samples are mainly calcite and gypsum. The gypsum fractions of the bulk analysis determined by the FY- and CEY-modes were almost identical i.e. ca. 15 mol%. The fact that the gypsum/calcite ratios are identical between the two modes for the bulk sample suggested that gypsum is not formed selectively at the surface of aerosol particles in the Aksu samples. Effect of difference in the particle size as a possible factor leading to the difference in mole ratios can be ignored here, because the samples were collected as a fraction with specific particle size (3.3–4.7 μm) by the size-fractionated sampling. The content of 15 mol% gypsum suggested here is reasonable, considering that gypsum is also found in the sands of the Taklimakan Desert as primary minerals, but its concentration is much lower than that of calcite.[15,16]

Similar results were obtained by μ-XRF-XAFS for individual particles. The XRF mapping illustrated distribution of single particles containing Ca on the carbon tape for the same aerosol samples collected in Aksu (Figure 1). Three particles were selected for the measurement of Ca K-edge XANES individually. Spectra of one particle measured in both FY- and CEY-modes are shown in Figure 2, along with the reference spectra of calcite, aragonite, and gypsum. The shapes of the XANES spectra measured in FY- and CEY-modes were almost identical
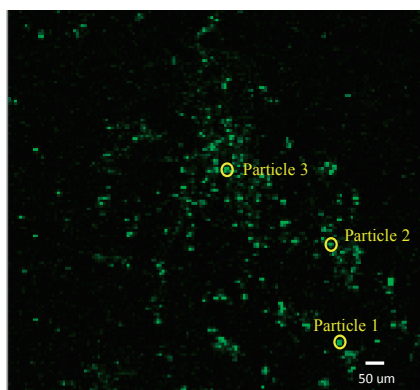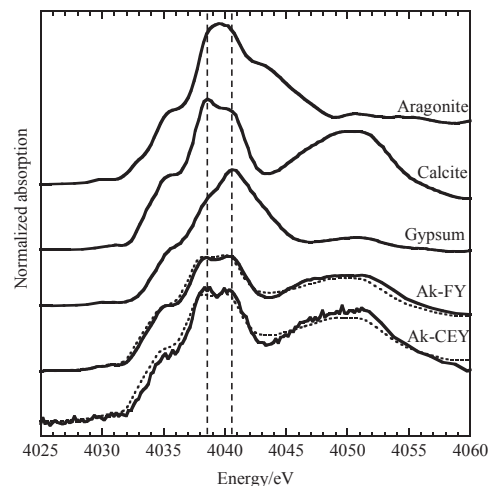

Figure 2. Normalized Ca K-edge XANES spectra of aerosol samples collected in Aksu (Ak) and the fitting line by least-squares fitting (dashed line). The spectra of reference materials (calcite, aragonite, and gypsum) are also shown.

to the spectrum of calcite. The least-squares fitting considering various Ca species including calcite, aragonite, gypsum, anhydrite, anorthite, dolomite, and apatite showed that these spectra of the aerosol samples can be fitted by assuming the two components, calcite and gypsum. The fitting results showed that the calcite fraction (f_{cal}) of the particle (Particle 1) was $f_{cal} = 86$ vs. 81 in the FY- and CEY-modes, respectively. Similar measurements for other two particles showed that $f_{cal} = 73$ vs. 78 in the FY- and CEY-modes, respectively, for Particle 2, and $f_{cal} = 100$ in both modes for Particle 3. The gypsum fraction is not large compared with those measured in Qingdao (mentioned below). In addition, the gypsum fractions were almost same between FY- and CEY-modes, showing that gypsum is not formed at the particle surface of calcite, but the two species are homogeneously mixed within each particle. These results suggested that (i) calcite in Aksu is not subject to neutralization during transport and (ii) small amount of gypsum relative to calcite may be directly transported from the Taklimakan Desert.

We also applied the same methods to the individual particles collected in Qingdao during the dust event. The result of average gypsum fraction by XAFS using mm-size X-ray beam for particles on the aerosol filter in FY- and CEY-modes were 37 and 55 mol%, respectively, for the particles having diameter 3.3–4.7 μm.[9] This result suggested that gypsum can be formed selectively at the particle surfaces, but it is not clear whether the neutralization reaction occurs at the surface of calcite, because a possible interpretation is that gypsum is simply coated on any particles. This ambiguity can be excluded using the depth-dependent μ-XAFS. Figure 3 shows Ca K-edge μ-XANES spectra for one aerosol particle collected in Qingdao with reference spectra of calcite, gypsum ($CaSO_4 \cdot 2H_2O$), and calcium nitrate ($Ca(NO_3)_2$). The result of μ-XANES in FY-mode showed that particles collected in Qingdao during a dust event consisted of calcite and gypsum (Figure 3). When we compared FY- and CEY-XANES spectra for the particle, we can find differences in the shapes of the spectra: the FY-XANES spectrum was similar to that of calcite, as seen from the shape around the peak-top. On the other hand, the shape around the
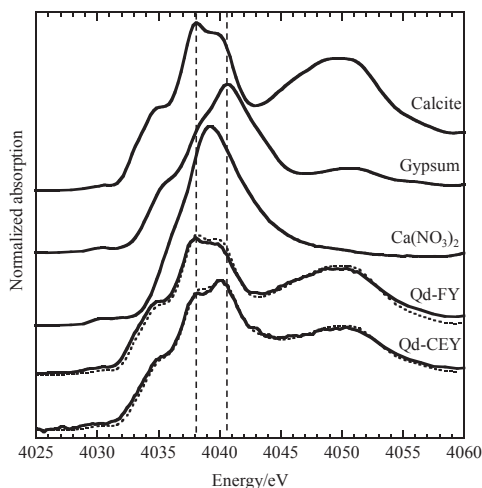

Figure 1. XRF-mapping of aerosol sample collected in Aksu. The sample collected on PTFE filter was dispersed on carbon tape employed for μ-XRF mapping, where green spots indicate intensity of Ca K line. Ca K-edge XANES of three particles (Particles 1 to 3) were measured.

Figure 3. Normalized Ca K-edge XANES spectra of aerosol samples collected in Qingdao (Qd) and the fitting line by least-squares fitting (dashed line). The spectra of reference materials (calcite, anhydrite, and gypsum) are also indicated.

peak top of the CEY-XANES spectrum shifted to higher energy than that of FY-XANES and the energy of the peak top at 4040.5 eV was almost identical to that of gypsum. f_{cal} was 70 vs. 43 in the FY- and CEY-modes, respectively, for Particle 1 in Figure 3. Another particle examined showed that $f_{cal} = 87$ vs. 55, respectively.

The results showed that the mole ratio of gypsum was larger in the CEY-mode than that in the FY-mode for individual particles, showing clearly that gypsum was mainly formed at the surface of the individual aerosol particles in Qingdao. In particular, coexistence of calcite and gypsum at different ratios in the bulk and at the surface of the particles in Qingdao suggested that gypsum was formed at the surface of the calcite particle during long-range transport from Aksu to Qingdao. Many previous studies reported that nitrate species can also be found on the mineral aerosol surface as well as sulfate.[17,18] Although fitting analysis conducted in this study included the spectrum of $Ca(NO_3)_2$, the mole ratio of $Ca(NO_3)_2$ obtained for the samples was less than 5%, which agreed with their bulk analysis of the samples.[9] The information of the reaction occurring on each particle surface cannot be obtained using mm-size X-ray beam, because the FY- and CEY-mode information provides average Ca species in the whole and surface of various particles, respectively.

The depth-dependent speciation using μ-XAFS in both FY and CEY modes directly showed that calcite was neutralized by sulfuric acid and transformed to gypsum at the surface of individual calcite particles in the atmosphere. This result was not clear in the reported study using bulk analysis. It is expected that this method will be a useful tool in future to understand chemical processes occurring at the surface of aerosols, which is important to elucidate the subsequent effect of aerosols in environment.

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