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A Study of the Chemical Processes in Aerosols and Their Impacts on the Environment Using X-ray Absorption Fine Structure Spectroscopy

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Introduction

The behavior of any elements in natural systems depend on their chemical states, such as their oxidation state, and chemical form in natural samples. Thus, speciation, or the identification of the chemical state, of elements has been investigated for various environmental samples. In particular, speciation in solid samples has not developed due to lack of appropriate methods to natural samples which are subject to their low abundances and interferences of various elements present in the samples. In addition, it is essential to analyze the samples under measurement conditions suitable for each sample so as not to alter the chemical species during the measurement, such as, for example, under ambient pressure. In this content, X-ray absorption fine structure spectroscopy (XAFS) has various merits that can solve the problems above (Tsuji *et al.* 2010).

Aerosols, small particles or droplets in the atmosphere, are produced from natural sources (e.g., mineral aerosols, sea salts, etc.) and from anthropogenic effects

(e.g., organic and sulfate aerosols). The chemical processes occurring in aerosols are complex, but most of the previous studies have speculated such processes based on the relative abundances of various chemical components in the aerosols. In this study, XAFS has been applied to the speciation of calcium, sulfur, zinc, and iron that are related to the neutralization of acid depositions, the cooling effect of the Earth, and nutrients to phytoplankton in the open ocean.

Study 1: Neutralization of Acidic Species in the Atmosphere by Asian Dust

Calcite, CaCO_3 , is abundant in Asian dust (around 10 wt.%), which is a compound reactive toward acidic species such as sulfuric and nitric acids. We employed X-ray absorption near-edge structure (XANES; XAFS consists of XANES and EXAFS (extended X-ray absorption fine structure) depending on the energy region within the XAFS spectrum) to determine calcium and sulfur species in aerosols (i) to obtain the ratio of calcite and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), the main calcium species

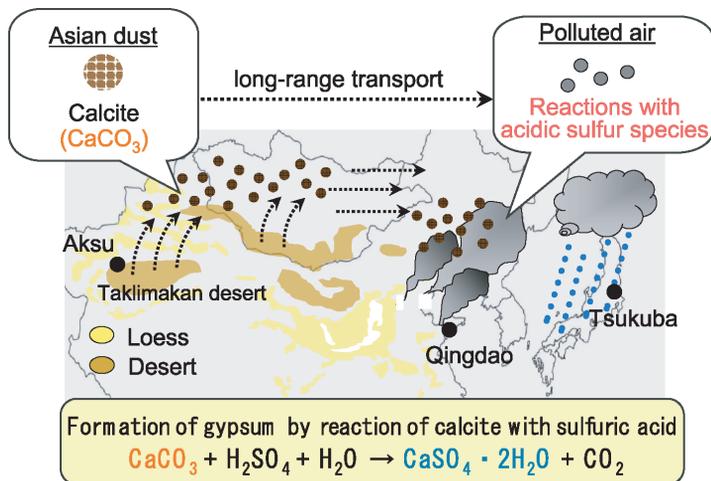


Fig. 1. Schematic of the neutralization process of calcite with acidic sulfur species during the long-range transport of Asian dust from Aksu to Qingdao and Tsukuba.

formed by neutralizing sulfuric acid in the atmosphere, and (ii) to identify calcium sulfite (hannebachite) in mineral aerosols. High-quality XANES spectra at the calcium and sulfur K-edge regions were obtained at beamline 9A at the Photon Factory (Tsukuba, Japan) using a He-purged chamber.

Calcium species in mineral aerosols collected simultaneously in Aksu (near the Taklimakan Desert), Qingdao (eastern China), and Tsukuba (Japan), during the Asian dust event in March 2002 and a nondust period in January 2002, were determined using Ca K-edge XANES (Takahashi *et al.* 2008, 2009). Locations of the sampling sites are shown in Fig. 1. From the fitting of XANES spectra, it was found that (i) calcite and gypsum were the main calcium species in the coarser particles ($>2.1 \mu\text{m}$) in the Asian dust samples, and (ii) the gypsum fraction versus the total calcium minerals $[\text{Gyp}]/[\text{Ca}^{2+}]_t$ increased in the order Aksu $<$ Qingdao $<$ Tsukuba in the coarser particles. Surface-sensitive XANES recorded in the conversion electron yield mode (CEY) showed

that the gypsum is formed selectively at the surface of mineral aerosols for all the samples, except for that collected in Aksu during the dust period. The decrease of the $[\text{Gyp}]/[\text{Ca}^{2+}]_t$ ratio with the increase in particle size showed that the neutralization effect proceeds from the particle surface. For the Aksu sample in the dust period, however, (i) the $[\text{Gyp}]/[\text{Ca}^{2+}]_t$ ratios obtained by XANES separately measured in the fluorescence (FL; regarded as bulk analysis) and CEY modes were similar, and (ii) size dependence was not found, showing that calcite is not neutralized for the 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 $(\text{NH}_4)_2\text{SO}_4$ to gypsum determined by sulfur K-edge XANES (Fig. 2; Takahashi *et al.* 2006, 2009) were positively, and negatively, correlated with the calcium (or calcite) content, respectively. The speciation of calcium by XANES revealed the neutralization processes of acidic sulfur species during the transport of mineral aerosols.

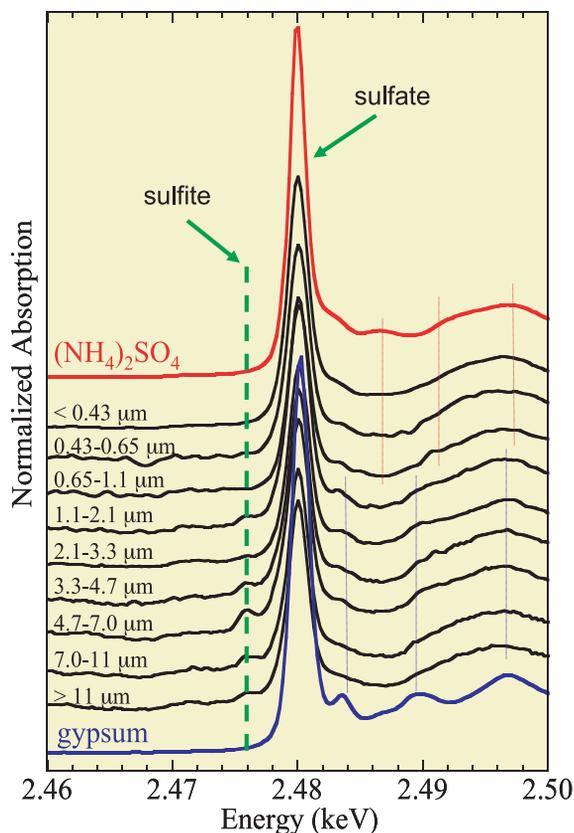


Fig. 2. Sulfur K-edge XANES for aerosols of various particle sizes collected in Qingdao in August, 2001. The spectra for gypsum and $(\text{NH}_4)_2\text{SO}_4$ were also shown. Peak position for sulfite species was also indicated.

Study 2: Effect of Metal Complex Formation on the Potential of Organic Aerosols as Cloud Condensation Nuclei

Although the XANES spectra of Ca in the aerosols can be explained by two components, calcite and gypsum, for particles above $2.1 \mu\text{m}$, we noticed that the aerosols at finer particle sizes ($<2.1 \mu\text{m}$) cannot be fitted by the two components, suggesting that other Ca species is present in the particles. Various references were included to fit the spectra of the finer samples, which suggests the presence of a Ca-oxalate complex in these samples.

It has been indicated in the IPCC report (IPCC 2007) that aerosols contribute to global cooling by direct and indirect effects. The latter effect is caused by the cloud-forming effect of hygroscopic aerosols, such as sulfate, and organic acid aerosols. Oxalic acid, the main component of organic aerosols in the atmosphere, is considered to contribute greatly to the indirect cooling effect, since it has a high hygroscopic nature, and can act as cloud condensation nuclei (CCN), as suggested in Kanakidou *et al.* (2005). We employed XAFS to determine Ca and Zn species in aerosols collected by size-fractionation air samplers in Japan. As a result, consider-

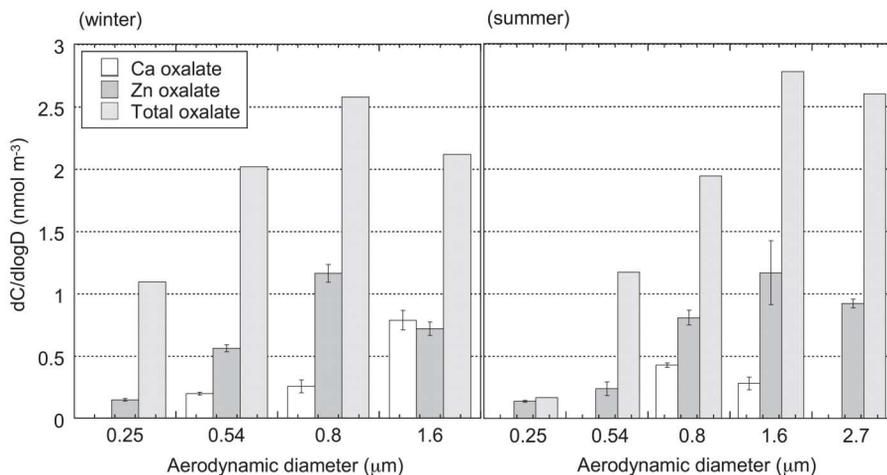


Fig. 3. Atmospheric concentrations of Ca oxalate, Zn oxalate, and total oxalate, during winter and summer of 2002 in Tsukuba.

able amounts of Ca and Zn were found to be present as metal-oxalate complexes in the aerosols at finer particle sizes ($<2.1 \mu\text{m}$). Taking into account the total amount of oxalate, and the possible contributions of other metal ions to the complex formation, it was suggested that most of the oxalate forms insoluble metal complexes (Fig. 3). As mentioned above, oxalic acid is hygroscopic and can thus increase the CCN activity of aerosol particles, while complexes with various polyvalent metal ions, such as Ca and Zn, are not hygroscopic, and cannot contribute to the increase of the CCN activity of aerosols. Based on the concentrations of non-complexed and metal-complexed oxalate species, we found that most of the oxalic acid is present as metal oxalate complexes in the aerosols (Fig. 3). These results suggest that oxalic acid does not always increase the hygroscopicity of aerosols in the atmosphere. Similar results are expected for other dicarboxylic acids, such as malonic and succinic acids. Thus, it is advisable that the cooling effect of organic aerosols should be estimated by including information on metal oxalate complexes

and metal complexes with other dicarboxylic acids in aerosols (Furukawa and Takahashi 2011).

Study 3: Evidence of Oxidation of SO_2 at the Surface of Mineral Aerosols

Sulfate aerosol is another important component that can be CCN in the atmosphere (IPCC 2007). Thus, the formation process of sulfate aerosols from SO_2 gas in the atmosphere is important in relation to its global cooling effect. Here, sulfur K-edge XANES was applied to the determination and quantification of tetravalent sulfur species in aerosol samples collected at Qingdao (Takahashi *et al.* 2006; Higashi and Takahashi 2009). Sulfite, tetravalent sulfur species, can be formed during the oxidation of SO_2 to sulfate, but the sulfite is usually regarded as an unstable species that can be finally oxidized to sulfate under the oxic condition of the atmosphere. However, XANES spectra showed that sulfite was found in particles with larger diameters (mineral aerosols) collected in August 2001 (Fig. 2). Two oxidation treatments in our experiments suggested that

calcium sulfite (CaSO_3 ; hannebachite) was the main tetravalent sulfur species in aerosols. No tetravalent sulfur species, however, were found at the surface of the aerosols as shown by surface-sensitive XANES detecting electrons emitted by X-ray irradiation using a conversion electron yield (CEY) mode. The presence of hannebachite in the interior of aerosols demonstrates the importance of heterogeneous oxidation of SO_2 : adsorption of SO_2 at the surface of mineral aerosols, such as calcite, with subsequent oxidation into sulfate species (Fig. 4). The fact that this process is supported from XANES analysis for natural samples is important as a chemical process in the atmospheric, because sulfite formed by the adsorption of SO_2 has only been detected in laboratory studies so far.

The contribution of heterogeneous oxidation to the total rate of SO_2 oxidation is not clear at present. However, this study suggests that (i) the adsorption of SO_2 on mineral aerosols without oxidation can reduce the oxidation of SO_2 in the atmosphere, especially in the presence of calcite, and (ii) the formation of hannebachite and, finally, gypsum by calcite reduces the formation of more hygroscopic sulfate species such as $(\text{NH}_4)_2\text{SO}_4$ which plays an important role as cloud condensation nuclei (CCN) for the cooling of the Earth by promoting the formation of clouds.

Study 4: Change of the Iron Species and Increase of Its Solubility during Long-Range Transport of Asian Dust

Iron (Fe) is an essential micronutrient and has been identified as a limiting factor for phytoplankton growth in high-nitrate low-chlorophyll (HNLC) regions of the ocean (Jickells *et al.* 2005). In the North Pacific, one of the HNLC regions, transport and deposition of mineral dust from Asia can be one of the major sources of Fe. In the atmosphere, Fe can be found

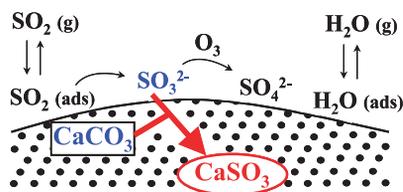


Fig. 4. Chemical processes of oxidation of SO_2 and formation of hannebachite at the surface of calcite.

and transported in a variety of chemical forms, both water-soluble and -insoluble. It is generally believed that only the soluble fraction of iron can be considered as bioavailable for phytoplankton. It is possible that only a part of Fe entering the ocean can be dissolved in the seawater depending on the Fe species. However, large uncertainties exist in the estimates of bioavailable Fe deposited from the atmosphere, owing to the wide range of Fe solubility in seawater. Photochemical processes, and the uptake of secondary acids and/or organics, can increase the solubility and bioavailability of iron in mineral aerosol particles, which is an important pathway for the fertilization of remote oceans with subsequent climate impact. Although it has been suggested that atmospheric processes can change the solubility of Fe as it moves from the source to the deposited area in oceans, the actual chemical processes affecting Fe species in mineral aerosols, such as Asian dust, are not clear. Thus, it is strongly suggested that the bioavailability of Fe is influenced by its solubility, or chemical species of Fe contained in Asian dust.

To assess the biogeochemical impact of the atmospheric input, an attempt was made to identify the Fe species by XANES (Fig. 5) and EXAFS. The speciation showed that chlorite, originally contained in the dusts, was selectively transformed into ferrihydrite during the long-range transport from Aksu to Qingdao and

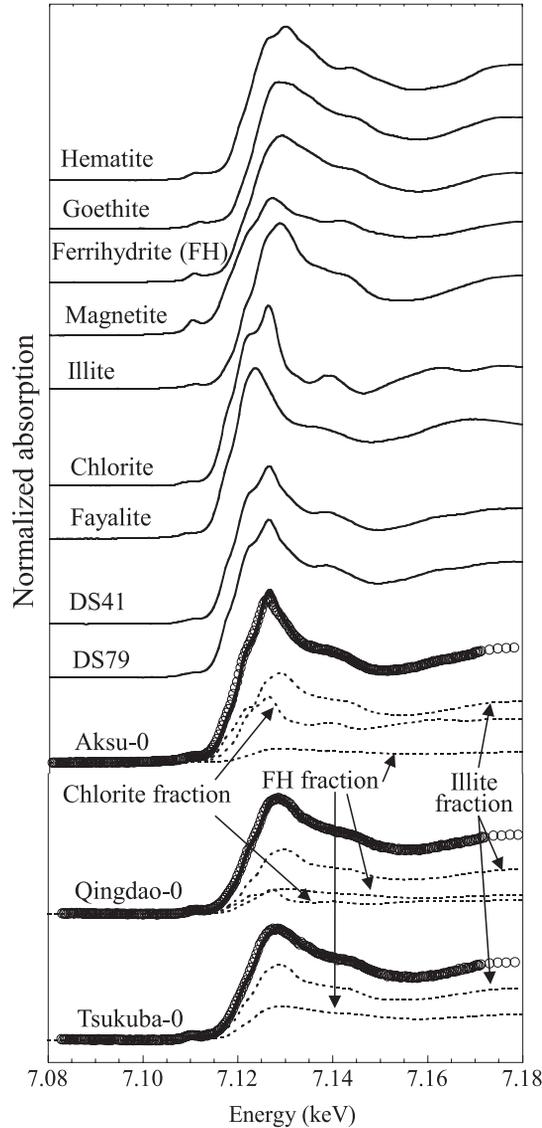


Fig. 5. Selected XANES spectra and the results of linear combination fit (LCF) for reference materials (hematite, ferrihydrite, magnetite (Fe_3O_4), illite (IMt-1), chlorite (CCa-2), and fayalite (Fe_2SiO_4)) and some Asian dust samples (Aksu-0 and Tsukuba-0). The sample name Aksu-0, for example, denotes that the sample was at stage 0 (particle diameter $>11 \mu\text{m}$ as shown in Methods) collected at Aksu. DS41 and DS79 are the spectra for Taklimakan Desert sands.

Tsukuba, in the event we studied. The high reactivity of chlorite, compared with illite, has been suggested in alteration experiments of the two minerals in mineralogical studies, which supports our results.

Surface sensitive CEY-XAFS also showed that the ferrihydrite fraction was larger at the surface of the aerosols, suggesting that the alteration process proceeds at the particle surface, as expected for reactions on

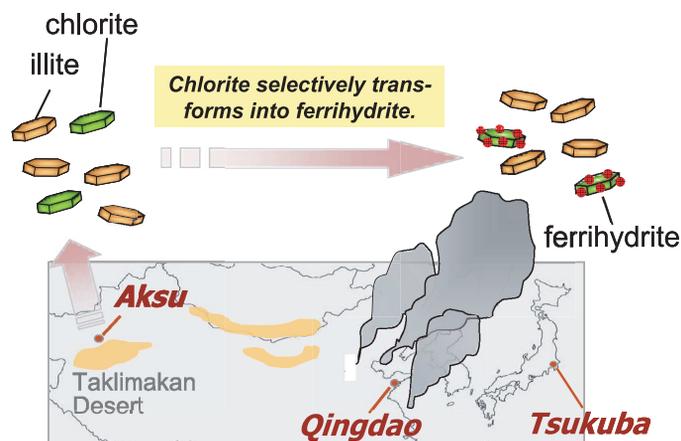


Fig. 6. Schematic of the change of iron species from illite and chlorite to illite and ferrihydrite during the long-range transport of Asian dust from Aksu to Qingdao and Tsukuba.

mineral aerosols in the atmosphere. Since alteration of calcite to gypsum, due to the reaction with sulfuric acid (Study 1), and also the enrichment of Pb in the finer particles were found in Qingdao and Tsukuba for the same samples examined here, it is suggested that the transformation of chlorite to ferrihydrite is facilitated by anthropogenic effects.

Moreover, leaching experiments were conducted for the natural dust samples with thorough information of the Fe species contained in the dust. As a result, we found that the original iron species near the source (western China) are clay minerals (illite and chlorite), which were transformed into ferrihydrite during long-range transport to eastern China and Japan by atmospheric chemical processes. In addition, iron in the dust becomes more soluble after transport, due to the formation of ferrihydrite.

Our findings demonstrate that ferrihydrite, secondarily formed during long-range transport, is a significant source of soluble Fe species (Fig. 6), which can control phytoplankton growth in the North Pacific (Takahashi *et al.* 2011).

Conclusions

Speciation of calcium, sulfur, and iron in aerosols determined by XAFS, gave the following results: (i) Asian dust containing calcite can contribute to the neutralization of acidic species in the atmosphere during the long-range transport from western China to Japan; (ii) the formation of various insoluble metal complexes for oxalic acid, suggesting that the role of CCN of oxalic acid can be lower than currently expected; (iii) the formation of sulfite species, such as CaSO_3 , and the subsequent oxidation of S(IV) species to sulfate, can occur at the surface of calcite, which must be considered as one of main formation processes of sulfate aerosols in the atmosphere; (iv) ferrihydrite secondarily formed in mineral aerosols during the long-range transport of Asian dust can be a significant source of soluble Fe species to the North Pacific, which can control phytoplankton growth in the area.

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References

- Furukawa F, Takahashi Y (2011) Oxalate metal complexes in aerosol particles: implications for the hygroscopicity of oxalate-containing particles. *Atmos. Chem. Phys.* **11**, 4289–4301.
- Higashi M, Takahashi Y (2009) Detection of S(IV) species in aerosol particles using XANES spectroscopy. *Environ. Sci. Technol.* **43**, 7357–7363.
- IPCC. Climate Change (2007) *Synthesis Report, the Intergovernmental Panel on Climate Change*. Cambridge University Press.
- Jickells TD, An ZS, Andersen KK, Baker AR, Bergametti G, Brooks N, Cao JJ, Boyd PW, Duce RA, Hunter KA, Kawahata H, Kubilay N, laRoche J, Liss PS, Mahowald N, Prospero JM, Ridgwell AJ, Tegen I, Torres R (2005) Global iron connections between desert dust, ocean biogeochemistry and climate. *Science* **308**, 67–71.
- Kanakidou M, Seinfeld JH, Pandis SN, Barnes I, Dentener FJ, Facchini MC, van Dingenen R, Ervens B, Nenes A, Nielsen CJ, Swietlicki E, Putaud JP, Balkanski Y, Fuzzi S, Horth J, Moortgat GK, Winterhalter R, Myhre CEL, Tsigaridis K, Vignati E, Stephanou EG, Wilson J (2005) Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.* **5**, 1053–1123.
- Takahashi Y, Kanai Y, Kamioka H, Ohta A, Maruyama H, Song Z, Shimizu H (2006) Speciation of sulfate in size-fractionated aerosol particles using sulfur K-edge X-ray absorption near-edge structure (XANES). *Environ. Sci. Technol.* **40**, 5052–5057.
- Takahashi Y, Miyoshi T, Yabuki S, Inada Y, Shimizu H (2008) Observation of transformation of calcite to gypsum in mineral aerosols by Ca K-edge X-ray absorption near-edge structure (XANES). *Atmos. Environ.* **42**, 6535–6541.
- Takahashi Y, Miyoshi T, Higashi M, Kamioka H, Kanai Y (2009) Neutralization of calcite in mineral aerosols by acidic sulfur species collected in China and Japan studied by Ca K-edge X-ray absorption near-edge structure. *Environ. Sci. Technol.* **43**, 6535–6540.
- Takahashi Y, Higashi M, Furukawa T, Mitsunobu S (2011) Change of iron species and iron solubility in Asian dust during the long-range transport from western China to Japan. *Atmos. Chem. Phys.* **11**, 11237–11252.
- Tsuji K, Nakano K, Takahashi Y, Hayashi K, Ro CU (2010) X-ray spectrometry. *Anal. Chem.* **82**, 4950–4987.