

## Detection of S(IV) Species in Aerosol Particles Using XANES Spectroscopy

X-ray absorption near-edge structure spectroscopy (XANES) at sulfur K-edge was measured to quantify S(IV) species in aerosol samples collected at Qingdao in northeastern China. The XANES spectra showed that sulfite was found only in particles with larger diameters (mineral aerosols). No S(IV) species, however, were found at the surface of the aerosols, as shown by surface-sensitive conversion electron/He ion yield XANES. The presence of hanebachite in the interior of aerosols demonstrates the importance of heterogeneous oxidation of  $\text{SO}_2$ : adsorption of  $\text{SO}_2$  at the surface of mineral aerosols such as calcite with subsequent oxidation. The chemical process of  $\text{SO}_2$  oxidation in the atmosphere and its implications were obtained based on the detection of sulfite species.

Recent atmospheric modeling studies have suggested that aerosol particles play a potentially important role in the chemistry of the troposphere by interacting with anthropogenic gaseous species such as  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ .  $\text{SO}_2$  can be oxidized to sulfuric acid and subsequently to various sulfate species in some processes. Such sulfate aerosols greatly influence the radiation balance and climate of the Earth, directly by scattering solar radiation and indirectly by serving as cloud condensation nuclei (CCN) having a cooling effect. Most  $\text{SO}_2$  is oxidized to sulfate either in the gas phase by OH radicals or in liquid droplets by ozone and hydrogen peroxide (Fig. 1). Model calculations suggest that aqueous phase oxidation is dominant on a global basis. In addition, heterogeneous uptake of  $\text{SO}_2$  on mineral particles such as calcite with subsequent oxidation has

been proposed in recent studies based on laboratory experiments. Although heterogeneous  $\text{SO}_2$  oxidation has been suggested in laboratory studies, intermediate S(IV) species which can form during the oxidation of  $\text{SO}_2$  to sulfate such as sulfite were not detected in previous studies. Thus, it is important to identify sulfite or other S(IV) species in natural aerosol samples because of their instability during analysis by some indirect methods and interference from other species in the samples. Thus, a direct method with high selectivity is essential to identify S(IV) species in natural aerosols such as by X-ray absorption near-edge structure spectroscopy (XANES).

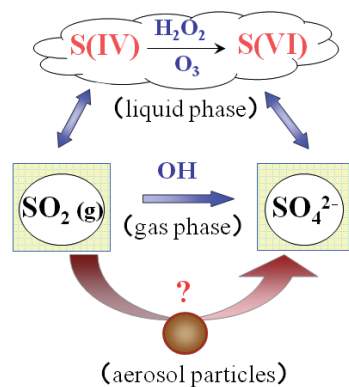


Figure 1  
Chemical processes of oxidation of  $\text{SO}_2$  in various phases in the atmosphere.

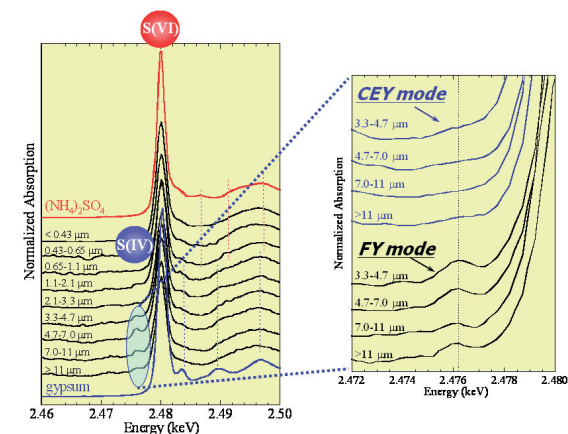


Figure 2  
Sulfur K-edge XANES for aerosols of various particle sizes collected in Qingdao in August 2001, measured in FY and CEY modes. The spectra for gypsum and  $(\text{NH}_4)_2\text{SO}_4$  are also shown. The peak position for sulfite species is also indicated.

Sulfur K-edge XANES for size-fractionated aerosol samples (9 fractions) were measured at BL-9A. The spectra showed that the major forms of sulfur in aerosols are sulfate, changing from  $(\text{NH}_4)_2\text{SO}_4$  to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  as the particle size increases (Fig. 2). The results are consistent with the fact that aerosol particles are suspended in an oxidative environment including OH,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ . However, a small amount of sulfite species was observed as peaks at lower energy than those for sulfate in XANES spectra (Fig. 2) measured in fluorescence mode (FY). In contrast, sulfite species were not found for the spectra measured in conversion-electron yield mode (CEY). The results showed that sulfite species are mainly in the interior of the particle, which suggests that  $\text{SO}_2$  had diffused to the particle interior prior to oxidation to form sulfite. Its stability upon heating to  $260^\circ\text{C}$ , its oxidation behavior after dissolution into water, and its presence only in mineral aerosols (coarser particles) indicated that the species is  $\text{CaSO}_3$ ,

hannebachite, formed in calcite. The presence of sulfite in mineral aerosols provides evidence that the oxidation of  $\text{SO}_2$  can occur also at the surface of aerosol particles. The contribution of heterogeneous oxidation to the total rate of  $\text{SO}_2$  oxidation is not clear at present. However, this study suggests that the adsorption of  $\text{SO}_2$  on mineral aerosols without oxidation can reduce the oxidation of  $\text{SO}_2$  in the atmosphere, especially in the presence of calcite.

### REFERENCES

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### BEAMLINE

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