

Interactive comment on “Composition and oxidation state of sulfur in atmospheric particulate matter” by Amelia F. Longo et al.

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We thank the reviewer for his/her very helpful comments and suggestions.

Reviewer 1 voiced concern about the potential effects of self-absorption for the sulfate standards, and requested further detail on the preparation of these standards. Sulfur standards were ground using an agate mortar and pestle to the consistency of a fine talcum powder (approximately 10 microns). A cellulose acetate filter was gently dredged through a small quantity (less than 1 mg) of powder placed on a microscope slide. This procedure produced a thin and almost imperceptible coating on the filter in order to limit the thickness and thus self-absorption. S-NEXFS spectra of sulfate standards were collected in bulk mode. Self-absorption must be carefully controlled when measuring fluorescent X-rays from thick specimens; however, the effects of self-

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absorption are limited to the region of the spectrum above the K-edge (Iida and Noma, 1993; Bajt et al., 1993). In our repeated measurements, the post-edge features were consistent and reproducible which allows us to distinguish between sulfate standards.

The energy was calibrated using an elemental sulfur standard (S0) measured at beamline 2-ID-B. The whiteness energy of the elemental sulfur standard was aligned to 2472 eV (Cozzi et al., 2009). All subsequent data uses 2472 eV as the reference energy for S0 during the data alignment mentioned by Reviewer 1. Furthermore, for every measurement two spectra are collected: the specimen and an aluminum sulfate standard on the monitor stick. This approach means that all spectra are referenced to the aluminum sulfate standard and the initial calibration is not as crucial on this beamline.

Reviewer 1 also wanted more detailed information to assist with the interpretation of the multi-energy maps presented in Figure S1. For the multi-energy maps, the units are raw counts from the detector. At this beamline, units such as mass per area are not provided. A more intense signal, that is the more counts present, indicates greater concentrations of sulfur in that region of the sample. The maps were generated at the whiteness energies of S0 and S+VI. The energies referenced in the methods are the actual settings used during experiment; in other words, these energies are not calibrated with the monitor stick. To identify the correct whiteness energies for the multi-energy mapping, a S-NEXFS spectrum was collected for the particle of interest immediately before mapping. The corresponding whiteness energies for S0 and S+VI were then taken directly off this spectrum. Individual maps were then collected at the whiteness energies determined for S0 and S+VI. Although it is possible that the energy drifted during mapping, the interval between the two measurements is short enough that this is not a problem. Due to the 6 eV difference in the whiteness energies of the S0 and S+VI oxidation states, we do not expect significant overlap between the two oxidation states in multi-energy mapping. Energy drift during mapping may reduce signal intensities of the S0 and S+VI oxidation states but the overall distribution patterns of the sulfur oxidation states in an individual particle should remain relatively unaffected.

C2

Fitting was not done to determine the relative abundance of sulfur at each oxidation state for each pixel. Instead, more accurate data from individual particle spectroscopy was collected and presented in the paper and supplement.

The reviewer also suggested that S-NEXFS data be provided in the supplement; therefore, additional figures will be added to the supplement that show exemplars of both the linear combination fitting and Gaussian peak fitting that were used to determine the sulfate composition and relative abundance of each oxidation state, respectively. These synchrotron-based measurements form the basis of this study. The concentrations of sulfur were not measured in this study.

All of the above information will all be added to the manuscript and/or supplement, should the paper be accepted.

We thank the reviewer for noting a few technical corrections as well. The reviewer is correct that the area of the Vortex SSD was 50 mm², and this will be corrected in the manuscript. Also, text referring to Figure S4 will be corrected to Figure S1.

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